ZEOLITES AS PARTICULATE MEDIUM FOR CONTACT HEATING AND DRYING OF CORN

A Thesis submitted to

The Faculty of Graduate Studies and Research of

McGill University

by

Zaman Alikhani

In Partial Fulfilment of the

Requirements for the Degree of

Doctor of Philosophy

Department of Agricultural Engineering

Macdonald College of McGill University

Ste-Anne-de Bellevue

Québec, Canada

ABSTRACT

Zaman Alikhani Ph.D. (Agric. Eng.)

Zeolites as particulate medium for contact heating and drying of corn

The potential of granular zeolites as a heating medium for drying corn was evaluated in a batch type experimental dryer. At temperatures from 150 - 250°C and residence times of 3 - 8 minutes, synthetic zeolites (4A and 13X) removed 9 - 18 percentage points from the initial moisture of corn. These values were about double those of sand, the most commonly used particulate medium.

Using an adiabatic dryer, the kinetics of moisture sorption in corn-zeolite mixtures was investigated. The heating medium in this part of the study was a natural zeolite (chabazite) and the corn was yellow dent type. Diffusivity values for corn were 1.012×10^{-5} - 3.127×10^{-5} cm^2/s with zeolite at temperatures of 140 - 220°C. These values are much smaller than those for zeolite. Therefore, it is believed that the diffusion of moisture in corn itself is the main resistance to the transfer of moisture. The heat transfer coefficient between corn and zeolite was found to be in the range of 50 - 312 $W/m^2 \cdot K$. Luikov's model for simultaneous heat and mass transfer was applied to corn-zeolite mixtures and the equations were solved by the Numerical Method of Lines (NMOL). These numerical solutions agreed closely with the experimental data.

The processed corn was subjected to *in vivo* and chemical analyses. Results of feeding experiments using laboratory rats did not indicate that the nutritive quality of the processed corn was adversely affected. Similarly, the acid detergent fibre analysis did not show a significant reduction in the availability of corn protein.

RESUME

Zaman Alikhani Ph.D. (Génie rural)

Les zéolites en tant que médium pour le chauffage par contact et le séchage du maïs

Le potentiel de granules de zéolite en tant que médium pour le séchage du maïs a été évalué. L'humidité extraite par la zéolite à des températures initiales de 250 et 150°C, respectivement, variait de 18 à 9 pourcent. Ces valeurs sont approximativement le double de celles obtenues en utilisant du sable, le médium granulaire le plus utilisé.

Les valeurs de la diffusivité effective de l'humidité dans le maïs étaient de 1.012×10^{-5} et de 3.127×10^{-5} cm^2/s, pour des températures initiales du médium de 140 et 220°C, respectivement. Ces valeurs sont de beaucoup inférieures aux valeurs correspondantes de la diffusion de l'humidité dans la zéolite aux mêmes températures. Par conséquent, la résistance principale au transfert d'humidité est certainement la diffusion de l'humidité dans le maïs. Le coefficient de transfert de chaleur entre le maïs et la zéolite se situait entre 50 et 312 $W/m^2 \cdot K$. Le modèle de Luikov pour le transfert simultané de chaleur et de masse a été résolu en utilisant la Méthode numérique des lignes. Les résultats de ces solutions numériques concordaient bien avec les données expérimentales.

Le maïs traité a été l'objet d'analyses in vivo et chimique. Les résultats des expériences de nutrition utilisant des rats de laboratoire n'ont pas montré que la qualité nutritive du maïs traité avait été négativement affectée. En outre, l'analyse au détergent acide des fibres n'a pas montré que la disponibilité des protéines du maïs avait diminué de façon significative.

This work is dedicated to

Mrs. Isabel Ruth Kindle

as a token of my deepest appreciation

for her friendship and for providing me and my family

with a home away from home.

ACKNOWLEDGEMENTS

I wish to express my gratitude to my academic supervisor, Prof. G.S.V. Raghavan, Department of Agricultural Engineering, McGill University. In academic support of his students, Prof. Raghavan goes well beyond the call of duty. As a caring teacher and an understanding friend, he gave me tremendous encouragement and confidence in my research.

Prof. A.S. Mujumdar, Department of Chemical Engineering, made a critical review of the manuscript and gave many valuable suggestions. Prof. E. Block, Department of Animal Science, was extremely helpful with planning the procedures for determining the quality of heat treated corn. I am indebted to Prof. S.O. Prasher, Department of Agricultural Engineering, for introducing me to the use of DSS/2 computer software and for his efforts in running the computer programs. I benefited a great deal from discussions with Prof. Eric Norris, Department of Agricultural Engineering.

Appreciation is expressed to professors at Macdonald College for being available whenever consulted. In particular, mention should be given to : Prof. S. Barrington, Agricultural Engineering; Professors Peter Schuepp, A.R. Godfrey, and N. Barthakur, Renewable Resources; Prof. M. Fanous, Plant Science; and Prof.I. Alli, Food Science and Agricultural Chemistry.

Financial support from the Natural Science and Engineering Research Council of Canada (NSERC), which made this research feasible, is gratefully acknowledged. McGill University also provided financial aid in the form of student loans and bursaries which is greatly appreciated. I would like to note my appreciation to Ms. Judy Stymest, International Students Advisor, McGill, for performing her duties graciously.

Dr T. Kudra, Post-doctoral Research Fellow, made available his equipment for measuring thermal conductivity of granular zeolite. He also translated several papers published in Russian. The Canadian Institute for Scientific and Technical Information (CISTI) provided many publications not available at McGill. Mrs. Tina Beals, Interlibrary loan librarian at Macdonald College, was extremely helpful in procuring these publications. I wish to thank her and all the library staff at Macdonald College.

During the course of this research, many individuals provided assistance in different ways. Messrs. R. Natress, technician, and R. Cassidy, Workshop supervisor, helped greatly in constructing the experimental setup. Mr. Al Barrington and Mr. Peter Kirby, provided corn for the experiments. Ms. Denise Gaulin helped with the Acid Detergent Fiber analysis. Fellow students, Miss Jocylin Ranger, Miss Rosidah Metussin, Messrs. Raymond Cholette, Mark McBratney, and M. Kabiri assisted with data collection and analysis in the laboratory; others who gave a helping hand at some stage of this study were Messrs. P. Norville, U.S. Sivhare, L. Tang, and P. Tarassof. Sincere appreciation is expressed to all of them.

Acknowledgement is due my Afghan friend, Mr. A. Qayoum Rezazada. He was a willing hand with everything from hand-shelling of corn to computer work.

My heartfelt appreciation to my brothers and sisters, back home in Afghanistan, who despite the hard times continued to encourage my studies.

Finally, my wife, Suyanee Vessabutr, was a great source of encouragement. Although a full-time graduate student herself, she always gave priority to my studies.

TABLE OF CONTENTS

List of Figures

Figure		Page

List of Tables

Nomenclature

A	a parameter which includes heat transfer through contact and the gas microgap; a constant
B_1, B_2	expressions in Eqn 4.5
C_o, C_1, ..., C_n	constants
C_p	heat capacity of solid material
D	diffusion coefficient
D_e	effective diffusivity of moisture in corn
D_o	constant in Arrhenius type relation
d	particle diameter
d.b.	dry basis
E	activation energy
H	latent heat
h	heat transfer coefficient
h_1	heat transfer coefficient between test particle and the adjacent bed particle in contact, based on the cross-sectional area of bed particle
h_r	heat transfer by radiation
J	flux
K_o, K_1	roots of the modified Bessel function
L	scalar quantity in Eqn 6.1; length of flat heat transfer surface in the direction of flow
L_1, L_2	parameters in Eqn 4.5
l	characteristic length; characteristic size of a pore
M_1, M_2	parameters in Eqn 4.5
m_1, m_2	parameters in Eqn 4.5
MGMR	medium-to-grain mass ratio
N_c	critical speed of rotation
n	number of particles in contact with the test particle
p	ratio of the volume of all solid particles to that of the total volume
q_n	roots of a transcendental function
$\mathcal{R}$	gas constant

R	radial coordinate
R_1	radius of the sphere immersed in a bed of granular material
r_o	radius of the bed particles
r	radial coordinate of bed particles
RH	relative humidity
s	local width of the gaseous gap
T	temperature
T_{mi}	Initial temperature of the heating medium
T_{ci}	Initial temperature of corn
t	time
U	moisture concentration at time t
U_∞	moisture content of a solid particle at very large values of t (in equilibrium with the surrounding medium)
V	volume
v	stream velocity of the moving body past flat surface
W.B.	wet bulb
w.b.	wet basis
X	gradient of potential
$X_1, X_2, ..., X_n$	dimensionless parameters.

Greek characters

α	thermal diffusivity
α_M	mass diffusivity
δ	thermogradient coefficient
ε	void fraction of a packed bed
ε_1	phase change criterion
ρ	density
λ	thermal conductivity
β	ratio of distance between centres of two neighboring solids to the particle diameter
Γ	ratio of the effective length of the solid particle to its diameter

χ	ratio of effective thickness of the fluid film adjacent to the particle surface and the particle diameter
ξ	parameter related to the thickness and width of the solid skeleton
ρ	bulk density of the granular material
μ_n	expression in Eq. 4.4
μ_1, μ_2	the first two roots of the transcendental equation
η_1, η_2	the first two roots of the transcendental equation
σ_0	mean free path of the gas molecules
γ	accommodation coefficient
ϕ	specific weight

Subscripts

A	air, gas, medium surrounding a spherical material
c	corn
eq	equilibrium
eff	effective
L	liquid
i	initial
p	particles
s	soild particles of spherical shape
V	vapor
z	zeolite

Dimensionless parameters

Bi	Biot number, $Bi = hl/\lambda_s$
Fo	Fourier number, $Fo = Dt/R^2$
Fr	Froude number, $Fr = v/(gl)^{1/2}$
Nu	Nusselt number, $Nu = hd/\lambda_A$
Pe^*	modified Peclect number, $Pe^* = (\lambda_s/\lambda_A)^2\ (d/L)^2\ Pe$
Pe	Peclet number, $Pe = vd/D$

CHAPTER ONE

PROLOGUE

If a man will begin with certainties, he shall end in doubts;
but if he will be content to begin with doubts he shall end in certainties.

— *Francis Bacon* (1561 - 1626)

1.1 Introduction

Timeliness of operations is the key to successful agricultural production. An important implication of timeliness is crop harvesting to minimize field losses. For corn, the recommended moisture contents of the grain to begin combining is 26-28 percent (Shove, 1970). This is well above the 13 percent mentioned as the safe moisture level for one-year storage of corn (Brooker et al., 1974). In some areas where temperatures during the harvest could be about 15-20°C (60-70°F), it takes only a few days before the grain spoils if not dried to a safe level; thus artificial drying is an integral part of the modern corn production process (Shove, 1970).

Drying is an energy intensive operation. The amount of heat required to dry a cereal grain depends on the latent heat of vaporization of water. The value of heat of vaporization is fixed for a particular grain temperature and moisture content (about 2330 kJ/kg, (Hall, 1980)). As stated by Peart and Lien (1975), it is unlikely that any new invention would change this physical phenomenon. However, improvements that can be brought about in terms of drying efficiency depend on improving the method of energy utilization, i.e. minimizing losses.

The most common method of drying grain is using oil- (or gas-) burning hot air dryers. By means of appropriate heat exchangers, or direct products of combustion, the air temperature is raised and the air is passed through the grain. This hot air serves as the heat and mass transfer medium for drying the grain. Keey (1972) and Foster (1973) have stated that using air as the only drying medium results in an inefficient process because the air will be saturated but use cannot be made of its sensible heat.

The drawback of losing the sensible heat of the exhaust air can be overcome by using a solid particulate medium (e.g. sand) which is heated and mixed with the grain, separated after grain drying and recirculated, resulting in a minimum loss of heat. Thus, with appropriate utilization of the sensible heat of the medium, some saving of the fuel required for drying is expected.

Aside from the possibility of enhancing the thermal efficiency of the process, another important aspect of using a solid particulate medium is the improvement in the rate of heat transfer. Compare to conventional drying, augmentation of the heat transfer coefficient due to a solid medium can be well over a hundred times. This in turn means that the use of granular materials as the medium of heat transfer can effect accelerated drying, and thus save considerable drying time.

Although there may be no need to overemphasize the importance of saving in drying costs, some statistics could be useful. It was stated by Keey (1972) that in the Soviet Union 15 percent of the total fuel produced was consumed for drying operations. It was estimated that in the United States alone about 3.8×10^6 m^3 (1.005×10^9 gallons) of liquid propane gas (LPG) were used for crop drying and over half of the energy consumption was for drying corn (Hall, 1980). In Canada, too, LPG was reported as the main source of energy for drying corn. In terms of percentage share of the sources of energy, LPG was 87 percent; electricity, wood, and other fuels accounted for the remaining percent (Statistics Canada, 1983).

There are also estimates for the drying cost as a percentage of total production costs. Fisher (1988) made a thorough breakdown of costs associated with the production of grain crops in the province of Ontario, Canada. In his analysis he included all likely costs, such as marketing board fee, crop insurance, interest on the material and miscellaneous. The cost of drying corn was reported to be about 10 percent of the total production cost. It can be said, then, that even a modest improvement in drying efficiency will result in considerable savings of fuel and resources.

Researchers in the past two decades have directed their efforts toward improving heat and mass transfer operations during grain drying. Their scientific studies have shown that sand, as the particulate medium for heat transfer, improves the heat transfer coefficient of the process. While heat transfer properties of sand are adequate, lack of optimum mass transfer properties makes sand less desirable. Since drying is a process of simultaneous heat and mass transfer, a breakthrough in improving the drying rate depends upon success in acquiring a medium which has both desirable heat and mass transfer properties.

This study deals with the evaluation of zeolites - a natural zeolite (chabazite) and synthetic zeolites (molecular sieves 4A and 13X) - as the drying medium. The results of drying experiments were studied with regard to the kinetics and dynamics of the process. And, finally, the processed grain was assayed for the nutritive quality of the product as a feed material.

1.2 Hypotheses

The main hypotheses of this study follow:

1. Application of zeolites as the heated particulate medium will enhance heat and mass transfer for grain drying.

2. Some combinations of temperature levels and duration of drying will result in adequate drying of the product.

3. Zeolites can be regenerated and re-used in a continuous process.

4. The quality of the product will not be affected by using zeolites as the drying medium.

1.3 Objectives

The main objectives of this research program were to study the following:

1. The potential of heated granular zeolites for drying grain corn.

2. The kinetics and dynamics of moisture sorption in a mixture of grain-desiccant, including an investigation of a mathematical model of the process.

3. Reactivation and the possibility of using zeolites in a continuous process.

4. Assessment of the quality of corn processed by mixing with granular zeolites.

1.4 Scope

In order to have better control over certain operating conditions, such as initial temperature of the heating medium and the residence time, drying experiments were performed in batch. The drying medium was placed in enamelled trays and heated in an electric oven rather than heating by flame, which is the case in the prototype continuous dryer.

The mass of moist corn in the drying experiments was 500 - 650 g. While this mass was adequate as far as the drying studies are concerned, the amount of corn processed was not sufficient for animal feed experiments using cattle. Therefore, the quality of the processed corn was determined by *in vivo* digestibility analysis using rats as experimental animals and by chemical analysis for the availability of the protein for digestion.

CHAPTER TWO

REVIEW OF LITERATURE

Knowledge is of two kinds. We know a subject ourselves,
or we know where we can find information upon it.

— *Samuel Johnson (1709 - 1784)*

The subject of this study is multidisciplinary and crosses several distinct areas of scientific research. It involves the application of conduction heating and drying, drying by adsorption using a desiccant, and the quality of heat treated corn. For the sake of clarity, the relevant literature is reviewed and presented in separate sections below.

2.1 Conduction Heating and Drying

Drying must have been one of the first processes man learned experientially. It is believed that the custom of slightly roasting cereals to improve their storage quality was practised in prehistoric times (Singer et al., 1958). In a chronology of the early use and development of drying, Kröll et al. (1980) stated that cereal grains were being dried by about 100 B.C. Keey (1972) remarked that kilns for drying grain were built in damp areas of Europe from the Iron Age onwards. The scientific study of drying is considered to have been begun by Van Helmant (1577 - 1644 A.D.), based on the record of his experiments (Kröll, et al., 1980).

While the history of what is considered as conventional air drying is well documented, similar records of the earliest use of a heated granular medium such as sand for drying do not appear to exist. However, it is well-known that for several generations people in Africa, India and the Middle East have used this technique for roasting grains. The scientific study of different aspects of drying with a heated granular medium began in the early 1970s. In the following conduction heating and how it led to the use of a granular medium are discussed.

The term conduction heating for grain drying is used when heat is supplied to a solid medium which comes in contact with the grain rather than to the air surrounding it. It appears that the earliest work on grain drying by conduction heating was reported by Kelly (1939). His dryer consisted of a drum rotating above a coal burning-furnace (Fig. 2.1).

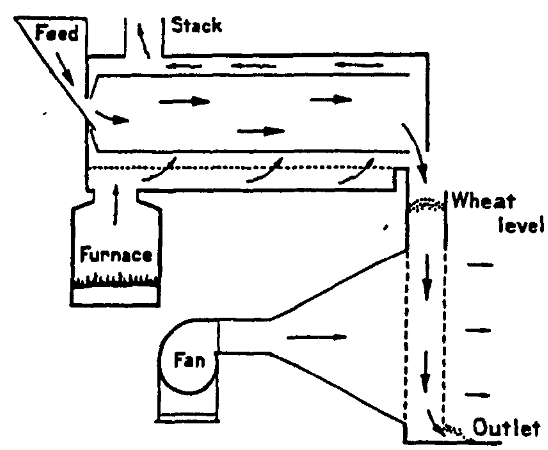


Fig. 2.1 Schematic diagram of an early conduction-heating grain dryer

(From Kelly, 1939)

Thus heating the grain (wheat) was performed mainly by conduction using the drum as the medium for heat transfer. The heated grain was then cooled by convection using an electric fan. The dryer had a capacity of 3.5 m^3/h (100 bu/h). Kelly (1939) commented that the quality of the processed wheat was satisfactory, but the amount of moisture removed was lower than required and therefore modifications were needed.

For several decades since Kelly's report, little work was done on the development of such dryers. Most of the subsequent papers on the subject area dealt with the theoretical aspects of the process.

Oxley (1948) referred to the conduction heating dryer as "a very popular and successful type of dryer." The dryer, he explained, consisted of hot metal surfaces on which the grain was passed and a counter current of air removed the moisture. He also stated that by using the hot-grain cold-air principle, if cool air stream is used, a large temperature gradient is created within the kernels, and therefore the movement of moisture within the grain is facilitated.

Hall and Hall (1961) compared the rate of drying corn by conduction and convection heating. Conduction heating and drying was performed by placing the corn kernels on a 1.02 mm (0.04 in) thick steel plate suspended above an electric hot plate; for convection heating the temperature of the forced air was the same as that of the steel plate. They concluded that conduction drying resulted in 10.2 - 16.5 percent saving in drying time for heating medium temperatures of 109 - 62°C (229 - 144°F), respectively.

Finney et al. (1963) studied conduction drying of shelled corn. Similar to Hall and Hall (1961), they achieved the heating of the grain by placing it on hot sheet metal. In their study they also included the effect of different air flow rates on drying time.

The overall thermal efficiency reported by Finney et al. (1963) was as high as 70 percent. While they had made provisions to minimize heat loss to the ambient environment, loss of heat in the exhaust air was inevitable.

Along the same lines, Chancellor (1968) proposed a grain dryer using conducted heat. The dryer consisted of a metal plate heated by straw. A blade was used for stirring the grain to prevent overheating by contacting the surface for long periods of time.

The use of a heated granular material, though not absolutely a new concept, was a major breakthrough. Researchers were justifying the use of this technique by objective reasoning and experimental data. Khan et al. (1973) clearly stated that by using a granular medium localized overheating of the product is prevented while conductive heat transfer is enhanced. About the same time, some other researchers also reported on grain drying by mixing with heated granular media (Iengar et al., 1971; Akpaetok, 1973; Raghavan, 1973; Lapp and Manchur, 1974).

The advantages of using a heated granular medium was established by then. Holt (1960) reported on the relative values of the coefficients for different modes of heat transfer and stated that the values of the coefficients increase from one for convective heat transfer to 20 for conductive, and 200 for contactive. Shabanov (1963) stated that the volumetric heat capacity of gases is about 1000 times smaller than those of solids, and a very large volumetric flow rate of gas or high initial gas temperature is required for heating a granular material. He remarked that mixing them with granules of a solid heating medium ensures a high rate of heat transfer.

From more recent publications it is possible to compare the coefficient of heat transfer for the specific case of drying corn. The heat transfer coefficient for drying shelled corn with air in the temperature range of 26.7 - 150°C has been reported as 52.3 - 59.3 $W/m^2 \cdot K$ (Fortes and Okos, 1981). Sibley and Raghavan (1986) reported on the surface heat transfer coefficient of corn immersed in a bed of heated sand. The overall heat transfer coefficient was observed to be as high as 250 W/m^2 K. This study included many factors such as medium-to-grain mass ratio and grain moisture content.

While researchers agree that using heated granular media enhances heat transfer, there seems to be less accord in employing the right stuff to achieve an optimum drying result. Therefore, researchers have experimented with a variety of solid materials as the medium for heat and mass transfer.

The choice of granular medium for heating has been as varied as the material being heated (dried) and the geographical location from which the researchers come. Raghavan and Harper (1974) used salt for drying corn. Mittal et al. (1985) used steel balls as the solid medium for heat transfer for drying wheat. Aguilera et al. (1982) employed heated ceramic beads for roasting navy beans. Arboleda et al. (1973) used sand for drying rice. The most commonly used medium reported is sand (Sibley and Raghavan, 1985; Lapp et al., 1977; Akpaetok, 1973; Khan et al., 1973; Iengar et al., 1971).

Sibley and Raghavan (1985) reviewed the parameters affecting grain drying when mixed with a heated bed of granular medium. They remarked that the amount of moisture removed depended on the type of grain, initial moisture content, medium-to-grain mass ratio, medium temperature and the duration of mixing (residence time).

Most of the scientific papers reporting on granular-medium drying had been at the test bench level. In order that this technique could be employed in real life, for grain drying on the farm, it was necessary to develop machines with reasonable drying capacities. Tessier and Raghavan (1984) and Pannu and Raghavan (1987) reported on two machines for continuous grain processing.

The grain processor developed by Pannu and Raghavan (1987), shown in Fig. 2.2, is a unique machine. It has an excellent thermal efficiency (70 - 90 percent). This machine can be efficiently used for heat-treating grains, e.g. heating of soybeans to degrade toxic factors, or for thermal disinfestation of a grain mass to eradicate insect population (Simonton and Stone, 1985). But, using sand as the medium of heat and mass transfer, as it was originally designed, does not result in adequate drying of corn to be considered safe for prolonged storage. The possibility of using some solid desiccants for improving the mass transfer property of the medium is discussed in the following sections.

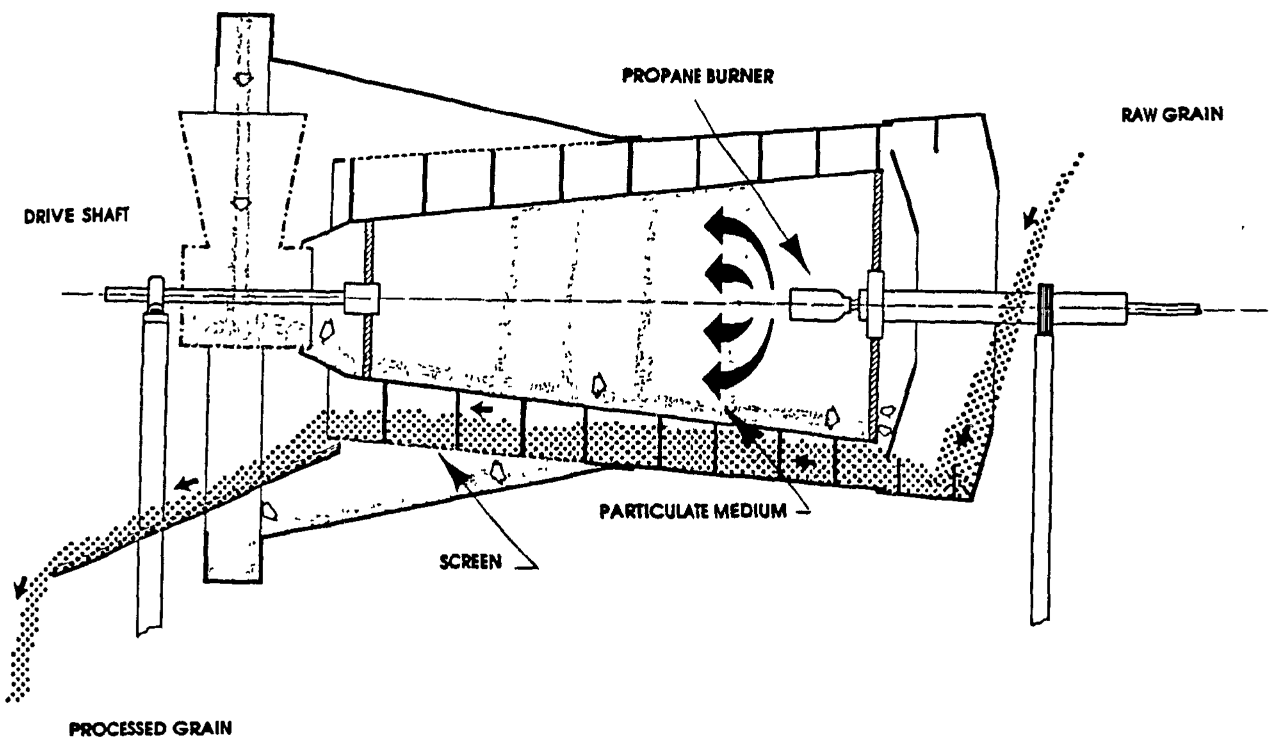


Fig. 2.2 Schematic diagram of the continuous flow particulate medium grain processor (*after* Pannu and Raghavan, 1987)

2.2 Heat Transfer Parameters

2.2.1. Thermal conductivity

It is discernible that the mechanism and rate of heat transfer through a solid material will be different from that of the same material with a gaseous interface, i.e. in the form of two contacting solid bodies. The thermal resistance through joints (Fig. 2.3) has been of particular interest in several areas of application of heat transfer, e.g. nuclear reactor, cooking on a hot plate, aircraft structural joints (Madhusudana and Fletcher, 1986). Because of the extensive volume of literature on the subject, the following review is limited to the thermal conductivity of granular materials.

Fig. 2.3 Schematic representation of heat flow through joints

(*from* Madhusudana and Fletcher, 1986)

It is generally accepted that the earliest scientific study of the thermal conductivity of granular materials was made by James Clerk Maxwell. Maxwell (1892) gave the following expression:

$$\lambda_{eff} = \frac{2\lambda_s + \lambda_A + p(\lambda_s - \lambda_A)}{2\lambda_s + \lambda_A - 2p(\lambda_s - \lambda_A)} \lambda_A \qquad \text{..............} \qquad (2.1)$$

where

λ_{eff} - effective thermal conductivity of the stagnant bed

λ_s - thermal conductivity of the solid material of spherical shape

λ_A - thermal conductivity of the medium in which the solid particles are placed

p - ratio of the volume of all solid particles to the total volume.

Maxwell (1892), however, did not use the term "effective thermal conductivity." Instead, he used "specific resistance of compound medium."

Rayleigh (1892) extended the work of Maxwell by including the effect of the thermal interaction of the surrounding spheres on the central sphere. Runge (1925), according to Meredith and Tobias (1960), modified the equation developed by Rayleigh. Meredith and Tobias (1960) further modified the Rayleigh equation. Their experimental data indicated that their modified version of the Rayleigh equation considerably improved the value of effective thermal conductivity over that obtained by the original Rayleigh equation.

It would be pertinent to mention that Russell (1935) used a different approach. He pointed out the importance of voids in insulating structures, such as bricks. His equation was based on an analogous electrical circuit for the thermal conductivity of granular material.

In recent times, several other models for effective thermal conductivity of granular materials have been published. One well-known model is that of Kunii and Smith (1960) whose general equation, after certain assumptions, e.g. neglecting contribution due to radiant heat transfer, reduces to the following equation:

$$\frac{\lambda_{eff}}{\lambda_A} = \varepsilon + \frac{\beta\,(1 - \varepsilon)}{\chi + \Gamma(\lambda_A / \lambda_s)} \qquad \text{............} \qquad (2.2)$$

where

β - ratio of distance between centres of two neighboring solids to the diameter of the particle

ε - void fraction of the packed bed

Γ - ratio of the effective length of the solid particle to its diameter

χ - ratio of effective thickness of the fluid film adjacent to the particle surface to the particle diameter.

Luikov and associates have also worked on the effective thermal conductivity of granular materials. The model given by Luikov et al. (1968) is as follows:

$$\frac{\lambda_{eff}}{\lambda_s} = \frac{1}{\left(\frac{\xi}{1+\xi}\right)^2 + A} + \frac{\lambda_A}{\lambda_s}\left(1 - \frac{\xi}{\xi+1}\right)^2 \qquad \text{.....................} \qquad (2.3)$$

where

ξ - parameter related to the thickness and width of the solid skeleton

l - characteristic size of a pore

A - parameter which includes heat transfer through contact and the gas microgap.

The models given by Kunii and Smith (1960), and that of Luikov et al. (1968), require experimental determination of certain parameters for each case. Moreover, these relations involve terms such as χ in Eqn 2.2, and ξ in Eqn 2.3, which are not easy to quantify. More recently, Dietz (1979) developed a model for effective thermal conductivity, which requires only knowledge of the thermal conductivity of the solid material and that of the fluid. The model which follows assumes that packing geometry is not critical:

$$\frac{\lambda_{eff}}{\lambda_A} = 1.14 \left(\frac{\lambda_s}{\lambda_A}\right)^{1/2} \frac{K_o\,[(40\,\lambda_A/\lambda_s)^{1/2}]}{K_1\,[(40\,\lambda_A/\lambda_s)^{1/2}]} \quad \text{..................} \quad (2.4)$$

where K_o and K_1 are the roots of the modified Bessel function.

Dietz (1979) stated that his model, which is independent of particle diameter, agreed favorably with published data in the range of $1 \leq \lambda_s / \lambda_f \leq 0.3 \times 10^3$.

2.2.1 Heat transfer coefficient

The theoretical basis for heat transfer between particles, whether in packed bed or in agitated state, is the same. Schlünder (1982) stated that when tackling the problem of heat transfer to moving beds, the problem is better divided into two parts: heat conduction and particle motion.

Several mathematical models describe the heat transfer coefficient, but only a few of the most pertinent studies will be reviewed in this section.

Harakas and Beatty (1963) reported on their study of heat transfer in a moving bed. Based on experimental results, they developed a relation for predicting the average value of heat transfer coefficient, h, which is as follows:

$$h = \frac{2}{\sqrt{\pi}} \left(\frac{\lambda_{eff}\, \rho\, C_p\, v}{L} \right) \quad \text{.....................} \quad (2.5)$$

where

ρ - bulk density of the granular material

C_p - heat capacity of the solid material

v - stream velocity of the moving body past a flat surface

L - length of flat heat transfer surface in the direction of flow.

They reported that with increased size of the bed particles and decreased bed thermal conductivity, the discrepancy between measured and predicted values became greater. They attributed the difference to the assumption that the bed was a homogeneous material.

One of the well-known studies on heat transfer coefficient for a flat plate immersed in a flowing granular bed is that of Sullivan and Sabersky (1975). They correlated their data by the following relationship:

$$Nu = \frac{1}{\chi + \frac{\sqrt{\pi}}{2}\sqrt{1/Pe^*}} \qquad \text{(2.6)}$$

where

$Nu = hd/\lambda_A$

$Pe^* = (\lambda_s/\lambda_A)^2 \, (d/L)^2 \, Pe$

$Pe = vd/D$

d = particle diameter

D - diffusion coefficient

and χ, the ratio of the thickness of the gas film to the particle diameter, was estimated to be equal to 0.085.

Richard and Raghavan (1980) studied heat transfer between a bed of granular materials and a heated spherical object, while the mixture is in motion in a rotating cylinder. The model consisted of a sphere immersed in the granular medium and the motion of the granular particles were considered to be that of free fall. The experimental part of the study involved the use of a stationary heated sphere, with provisions for temperature measurement and a channel through which the granular material fell on the sphere. The flow of particles past the sphere was schematized as given in Fig 2.4.

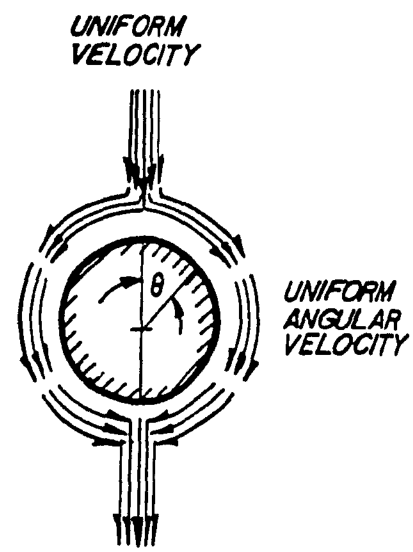


Fig. 2.4 Flow of particles past a sphere

(*from* Richard and Raghavan, 1980)

These authors stated that one parameter of importance for this type of heat transfer is χ, when the contact time is small. They arrived at the following relation for χ:

$$\chi = 5.16\ \varepsilon^{5.06} \qquad \text{......................} \quad (2.7)$$

Schlünder (1981) based his analysis of heat transfer from a bed of particles to a submerged surface on heat conduction through the gas film, which separates the particle from the wall. The relation for the heat transfer coefficient between particles and the surface was given as:

$$h = \frac{\lambda_A}{s + \sigma} + h_r \qquad \text{......................} \quad (2.8)$$

where

$$\sigma = 2\,\sigma_0\,\frac{2 - \gamma}{\gamma}$$

σ_o = mean free path of the gas molecules

γ = accommodation coefficient

s = local width of the gaseous gap

h_r = heat transfer by radiation

Schlünder (1981) provides the numerical values of the parameters for certain cases. The heat transfer coefficient between a sphere of 1 mm diameter and a smooth surface for dimensionless radius (x/R) from 0 - 0.5 was reported to be in the range of 0 - 3750 $W/m^2{\cdot}K$.

Rao and Toor (1984) studied heat transfer from a hot sphere to the surrounding bed of particles. They stated that the continuum approach for heat transfer will give satisfactory results if the hot particle is much larger than the bed particles. Rao and Toor (1987) developed a relation for heat transfer coefficient to take into account the effect of size and thermal conductivity of a sphere (referred to as test particle) and the surrounding bed of particles. The relationship is as follows:

$$h = \frac{\lambda_{eff}}{R_1} \Big/ \left\{ \left[\left(\frac{h_1 \, n \, r_o^2}{\lambda_{eff} \, 4 \, R_1}\right) + \left(1 + \frac{R_1}{r_o}\right) \frac{\varepsilon \, \lambda_A}{\lambda_s} \left(1 + \frac{h_r \, 2 \, r_o}{\lambda_A}\right)\right]^{-1} - \frac{r_o}{R_1 + r_o} \right\} \qquad \text{.....................} \quad (2.9)$$

where h_1 - heat transfer coefficient between test particle and the adjacent bed particle in contact, based on the cross-sectional area of bed particle

n - number of particles in contact with the test particle

R_1 - radius of the test particle

r_o - radius of the bed particles surrounding the test particle.

The physical circumstances under which Rao and Toor (1987) derived the equation were those of a sphere immersed in a packed bed. One study which tackles the problem of heat transfer coefficient during the drying of corn by mixing it with granular materials is that of Sibley and Raghavan (1986). They used a multiplicative power model, suggested by Downs et al. (1977), which has the following form:

$$Nu = C_o \, (X_1)^{C1} \, (X_2)^{C2} \ldots (X_n)^{Cn} \qquad \text{..................} \quad (2.10)$$

where C_o, C_1, ..., C_n are constants and X_1, X_2, ..., X_n are dimensionless parameters.

Deriving the dimensionless terms they arrived at an empirical relationship for the heat transfer coefficient during the drying of corn given as:

$$Nu = 2.4899\ (Fo)^{-0.4076}\ (MGMR)^{0.3769}\ ((T_{mi} - T_{ci})/T_{mi})^{1.4357} \quad \ldots\ldots\ldots \quad (2.11)$$

where Fo - Fourier number

T_{mi} - initial temperature of the heating medium

T_{ci} - initial temperature of corn

MGMR- medium-to-grain mass ratio

2.3 Solid Desiccants for Drying

Close and Dunkle (1970) suggested that the use of a desiccant, such as silica gel, can be a good means of storing solar energy. They also pointed out the benefits of reduced importance of insulation for this type of thermal energy storage. One major area of application of solar energy in food production and processing, namely crop drying, is hampered by the intermittent nature of the availability of this resource. To overcome this problem, best use can be made of this resource by incorporating means of storing it. There are numerous articles on the application of desiccant materials for dehumidifying air, which is then used for drying wet objects. An extensive review of the literature is given by Miller (1984). The papers on desiccants mentioned below are pertinent to the mixing of a solid desiccant with a wet solid to be dried.

Danziger et al. (1972) reported on drying corn by mixing with silica gel. The intimate mixture with a ratio of 1:3 (silica gel : wet corn) resulted in 10.3 percent moisture loss within 24 h for corn with an initial moisture content of 24.7 percent (w.b.). Chung and Fleske (1973) and Hsiao (1974) studied grain drying and prevention of dried-grain spoilage in storage, using silica gel.

Silica gel is not the only desiccant for storing energy that appears in the literature. Sturton et al. (1983) and Graham et al. (1983) reported the use of desiccant bentonite for grain drying. However due to its relatively low adsorption capacity, a large amount of bentonite will be needed. Graham et al. (1983) indicated that with 1:1 initial grain mass to initial bentonite mass, the moisture content of corn dropped from 30 percent (w.b.) to 17.5 percent (w.b.) in 24 h. Graham and Bilanski (1986) remarked that for drying corn to a safe moisture content for storage, the ratio of corn to bentonite (regenerated to 7 percent d.b.) should be of the order of 0.5.

Static mixing of the solid desiccant materials with grains is an excellent way of utilizing stored solar energy but the process is slow and, as indicated above, the major part of moisture from the grain is removed in periods longer than 24 h. Therefore desiccants such as silica gel and bentonite are not optimal media for accelerated drying of grains.

The mixing of heated silica gel or bentonite with moist corn will enhance the moisture diffusion in the grain due to the increased temperature but the adsorption capacity of these desiccants will be drastically diminished. Flanigan (1984) observed that the water adsorption capacity of silica gel dropped from 25 percent at about 15°C to almost nil when the temperature increased to 65°C. On the other hand, she reported that molecular sieve zeolites retained some water adsorption capacity up to 260 °C (Fig. 2.5). Thus zeolites come into the picture. Because of the importance of zeolites in this study, the literature pertinent to zeolites is reviewed in a separate section.

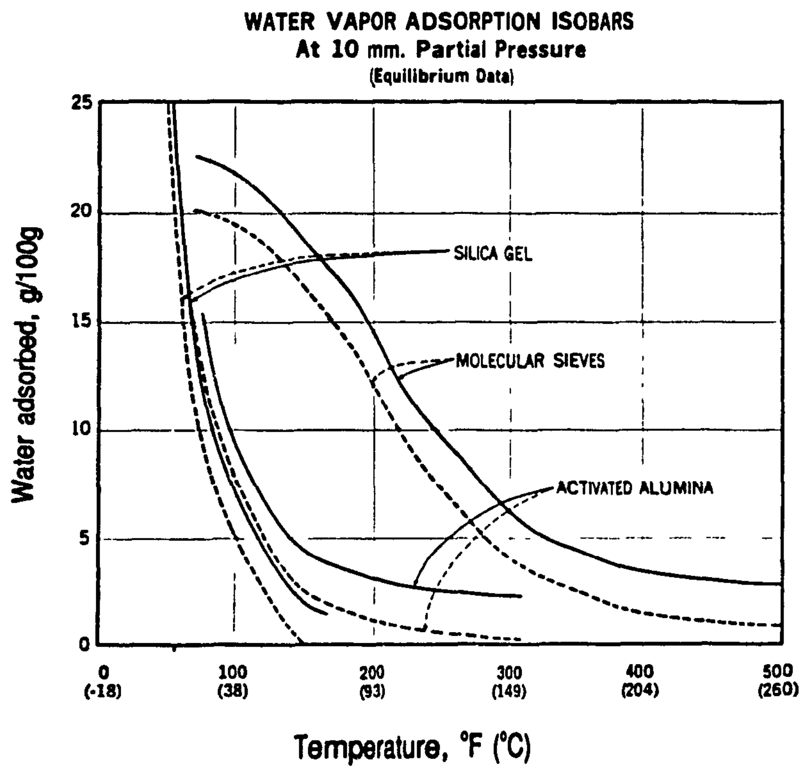


Fig. 2.5 Comparison of water adsorption capacity of zeolite and other desiccants (Union Carbide, 1983)

2.4 Zeolites

2.4.1 General

The term zeolite, from Greek ζειυ meaning to boil and λιθοσ meaning stone was coined by Cronstedt in 1756 when he observed that this mineral expelled water and seemed to boil (Gottardi, 1978). Zeolites are a group of minerals characterized by reversible loss and gain of water without significant structural deformation (Mumpton, 1984).

Zeolites are also manufactured. Synthetic zeolites are also referred to as molecular sieves. There are a large number of synthetic zeolites whose natural counterparts are not yet known, and conversely many natural zeolites are not yet manufactured (Breck, 1980).

Zeolites are micropore-adsorbent, and all pores are filled at very low relative pressure of adsorbate. Zeolites belong to type I of the Braunauer, Emmett, and Teller (BET) classification.

Zeolites structure contain several types of building units:

(i) primary units: tetrahedron of four oxygen ions with a central tetrahedral ion of Si or Al

(ii) secondary building units: single or double rings

(iii) larger symmetrical polyhedra.

A ball-and-stick model of tetrahedral coordination of oxygen ions with aluminium and silicon as the building blocks of zeolites and a skeletal model for molecular structure of chabazite are given in Fig. 2.6.

Zeolites have many uses. Mumpton (1978) discusses in detail several uses of natural zeolite and its significance as a new industrial mineral commodity for applications

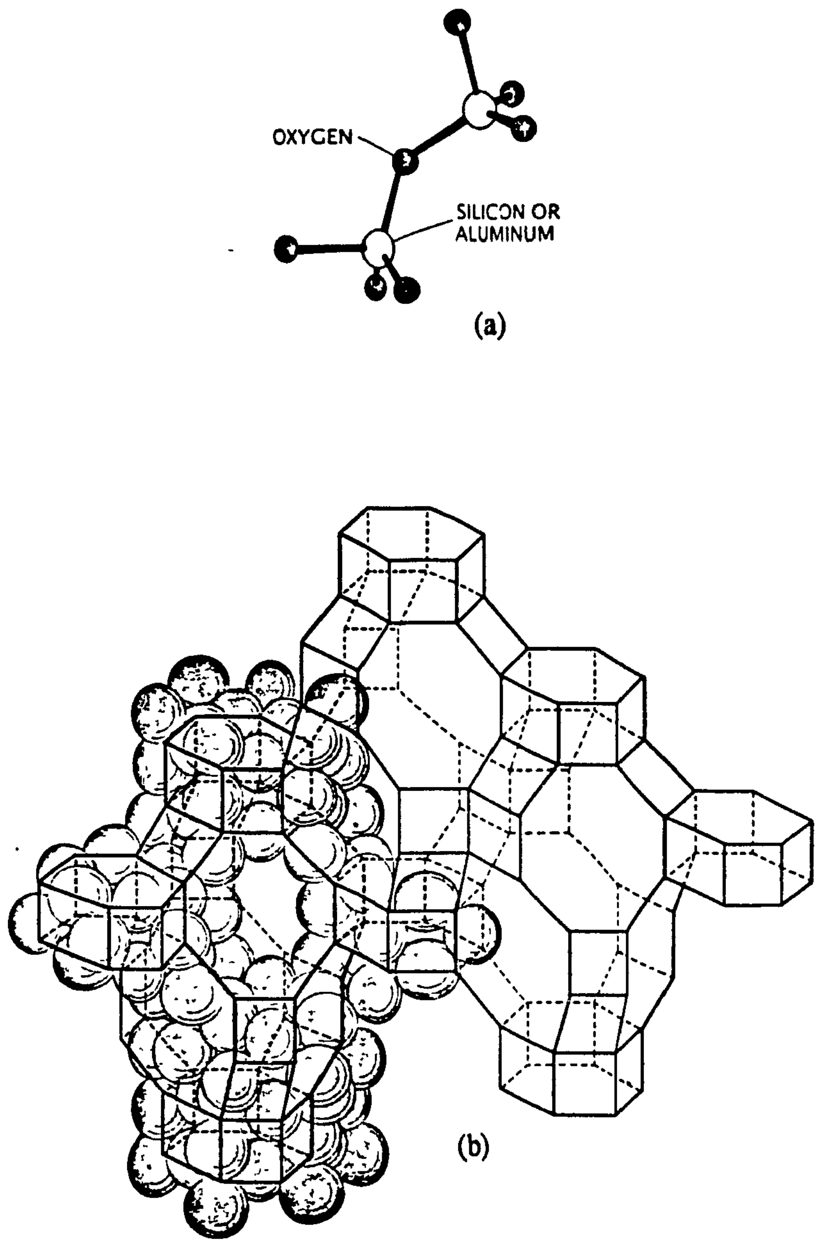


Fig. 2.6 Molecular structure of zeolite (a) Tetrahedral coordination of oxygen ions with aluminium and silicon (*from* Kerr, 1989). (b) A skeletal model for chabazite structure (*from* Breck and Smith, 1959)

ranging from oil-spill cleanup to polishing agent in fluoride-containing toothpaste. The application of molecular sieves in the chemical industry includes drying air and other gases. In the agricultural industry the use of zeolite is reported for waste treatment. No publication on the use of zeolites for grain drying was found in the literature.

2.4.2 Zeolites and Animal Nutrition

The unique properties of zeolites have resulted in a variety of applications of this material. Zeolites have been included in the diets of several species of animals and the latter's responses studied.

Mumpton and Fishman (1977) reported improved body weight gain and efficiency of feed utilization due to supplemental diets of natural zeolites for swine and poultry. Ma et al. (1979), cited by Ma et al. (1984), reported that a diet containing 5 percent clinoptilolite for pregnant sows resulted in an increased litter size at birth.

Vruzgula and Bartko (1984) studied the effects of feeding 5 percent supplemental clinoptilolite diet. Their study showed increased weight gain as compared to the control animals. They also mentioned that the addition of clinoptilolite in the diet did not show unfavorable effects on the liver function of the experimental animals.

Raetaskaya (1987) attributed the beneficial effects of diets for growth of animals to "their ability to bind metallic cations rendering them more available to animals." He also pointed out that zeolites can absorb toxic products of digestion and thus decrease the accumulation of toxic substances in tissues.

Nestrov (1984) extensively studied the effect of zeolite in the diets of beef cattle, sheep, pigs and poultry. Improved weight gain was reported for the inclusion of zeolite in the diets of all animals studied. Evaluation of the meat from these animals did not show any detrimental effect on quality.

Sweeny et al. (1984) stated that the improvement in nitrogen, organic matter and acid detergent fibre digestibility was achieved when 5 percent clinoptilolite was added to the diet of growing steers and heifers.

The effect of the zeolite ration on the quality of milk was studied by Garcia-Lopez et al. (1988). They reported positive results due to a dietary supplement of a natural zeolite.

Not all reports have shown improvement in the weight gain due to a diet of zeolite, however. Mumpton (1984b) reported on his personal communication with G.H. Arscott of Oregon State University that he observed slightly less weight gain for broiler chicken fed a diet of 5 percent clinoptilolite than those on the normal diet. However, he had noticed an increase in apparent feed efficiency and a decrease in mortality rate due to the zeolite diet.

Clinoptilolite is by far the most abundant type of sedimentary zeolites (Hawkins, 1984) and its availability could be the main reason for its widespread use in animal nutrition studies.

White and Ohlrogge (1974) reported on the effect of introducing natural and synthetic zeolite into the rumen of the animals under study. They stated that the "take-up of ammonia by the cation exchange zeolite during the fermentation period permits the addition of supplemental nitrogen to the animal feed while protecting the animal against the production of toxic levels of ammonia."

Synthetic zeolites, because of their application and importance in industry, have also been the subject of studies on the health and safety of animals exposed to this substance. It is reported that an intake of 5 g kg^{-1} body weight by rats did not produce any ill effects; rats have been shown to survive doses of 32 g kg^{-1} body weight (Breck and Anderson, 1981).

2.5 Quality of Heat-Treated Corn

Quality is generally considered as the degree of excellence but in a broad sense, as used in quality control, it represents the specifications to be met within the tolerance limits (Kramer and Twigg, 1970). Thermal processing of corn will result in some changes in its properties and end use will determine whether these changes are beneficial or not. About 90 percent of corn harvested in the United States (Bakker-Arkema et al., 1978) and 85 percent of corn produced in many other countries (Watson, 1982) is used for animal feed. A review of the literature on the effect of thermal processing on corn's quality as a feed material follows.

Cabell et al. (1958) reported that prolonged heating of corn at temperatures above 57°C to dry grain decreased the nutritive value of corn proteins for rats. However, they remarked that heating at temperatures as high as 116°C for shorter periods of time (2.5 h) did not have detrimental effects. Muhlbauer and Christ (1974), cited by Bakker-Arkema et al. (1978), studied the effect of kernel temperature and the duration of exposure to that temperature on the nutritive value of corn. Rapid drying at 180°C (7 min) resulted in a better quality than grain dried at 140°C for 21 min or 160°C for 14 min.

Hathaway et al. (1952) studied the effect of seven temperature levels (room temperature to 115.6°C) on drying high-moisture corn. They reported significant differences in the response of animals in terms of weight gain. Emerick et al. (1961)

reported on drying high-moisture corn using air temperatures up to 232°C. While corn dried at 177 and 232°C showed considerable damage, the performance of experimental animals was not affected by the drying temperature as much as indicated by Hathaway et al. (1952).

Sullivan et al. (1975) extensively studied the effect of feeding heat-treated corn on the weight gain and gain-to-feed ratio efficiency of 72 yearling Holstein steers. The trials included feeding non-treated and corn treated at 83, 104, and 127°C (grain temperature). They reported that average daily gains were not significantly different but feed efficiency increased linearly with increased temperature.

It is known that the nutritional requirements of livestock are different as, also the animals' response to processed grain. Church (1984) stated that ample evidence exists to show that heating of cereal grains result in more efficient utilization of the feed by ruminants. Hatfield and Wilson (1973) stated that if thermal processing causes heat damage to corn protein, the availability of aminoacids for non-ruminants will be more affected than that for the ruminants.

Hatfield and Wilson (1973) remarked that the drying temperature, at some level, will have a measurable effect on the nutritive value of corn. They added that the adverse effect of extreme drying temperatures can be minimized by reduced exposure time.

CHAPTER THREE

EVALUATING MOLECULAR SIEVES FOR CORN DRYING

It is hard to make a good theory - a theory has to be reasonable but a fact doesn't.

— G.W. Beadle (1903 -)

3.1 Introduction

Enhancement of heat transfer as a result of using a solid particulate medium is well established. Researchers have experimented with several materials to find the optimum medium for grain drying. There are numerous papers with satisfactory results on grain drying using heated sand as the medium of heat transfer.

As mentioned in Section 2.5, molecular sieves have many uses in the chemical industry, especially in separation processes by removing moisture from gases. The application of molecular sieves for drying grains may have been avoided for the fear of contaminating the crop, although up to 2 percent aluminosilicate is allowed as food additive in the GRAS (Generally Recognized As Safe) list of the United States Food and Drug Administration (Furia, 1980).

The effect of drying corn with heated granular zeolite on the quality of processed grain will be discussed in Chapter Seven. This chapter deals with the potential of molecular sieves (synthetic zeolites) in terms of the amount of moisture removed from the moist grain. In these studies, sand is also used under similar operating conditions and the results are compared with those of molecular sieves to evaluate their potentials for grain drying.

3.2 Materials and Methods

3.2.1 Experimental Materials

Two types of particulate media were used: molecular sieves and sand. Synthetic zeolites (molecular sieves) were selected for their uniformity, thermal stability and high moisture adsorption capacity. Sand was chosen because of the numerous papers on using heated sand for grain drying with satisfactory results. The molecular sieves were of two types, 4A and 13X. Type 4A was used in two sizes: 8 - 12 mesh (1.7-2.4 mm) and 14 - 30 mesh (0.6 - 1.4 mm), whereas type 13X was of 8 - 12 mesh size and in powder form. Sand passing 0.5 mm and retained on a 0.3 mm screen was used. Preliminary studies with the powdery 13X zeolite showed that the processed corn was coated with the zeolite, and proper mixing of the grain and zeolite was a problem. Therefore, the idea of using powdered zeolite was dropped. In all, four media were used in this part of the study if account is taken of the molecular sieve types and sizes.

The unit cell formulas of the molecular sieves (Union Carbide, 1983) are as follows:

$$\text{Type 4A} \quad Na_{12}[(AlO_2)_{12}\,(SiO_2)_{12}]\;27\;H_2O$$

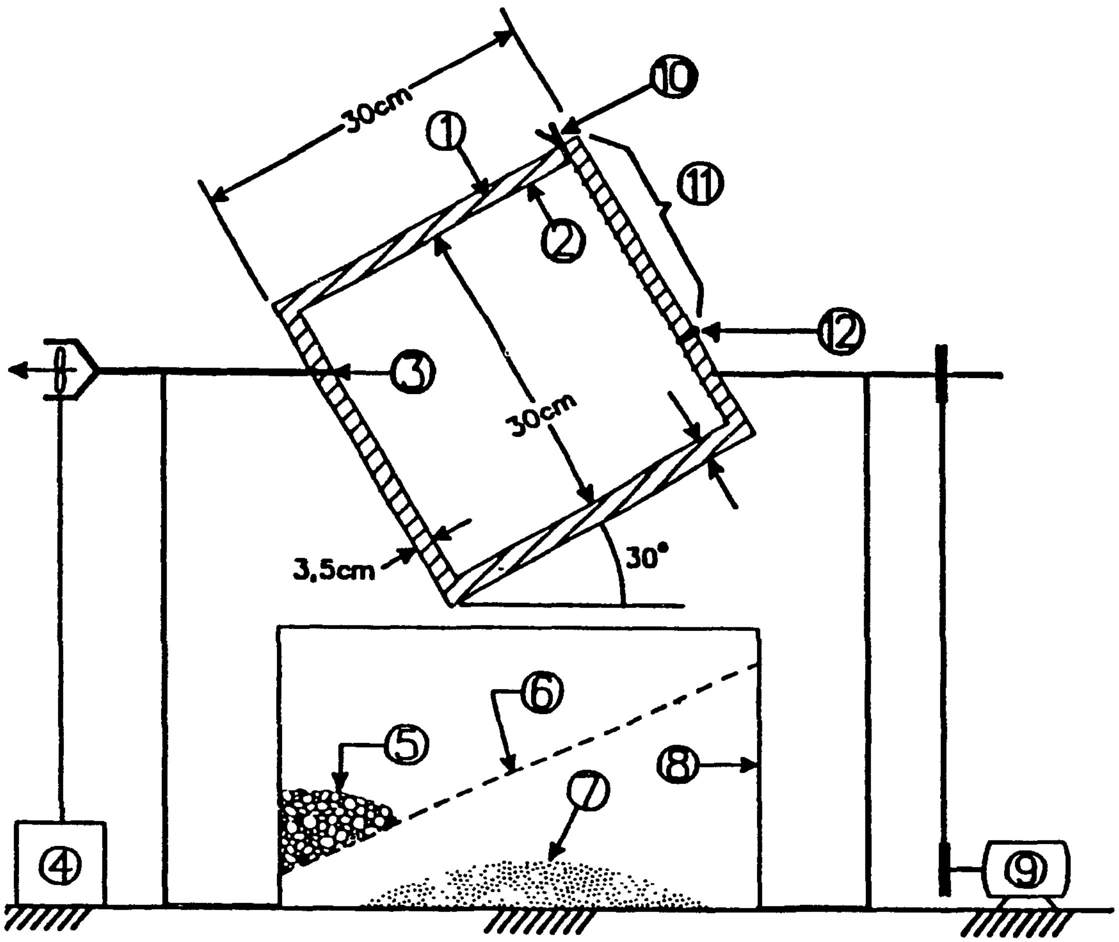
$$\text{Type 13X} \quad Na_{86}[(AlO_2)_{86}\,(SiO_2)_{106}]\;276\;H_2O$$

The dryer, which rotated about an eccentric axis, was designed for batch processing. A schematic diagram of the dryer is given in Fig. 3.1. The dryer was insulated inside by 3.2 mm thick teflon and outside by fibreglass. Cylinder rotation was done by coupling with a variable-speed AC motor.

A quick-release door facilitated the flow of the mixture to separate the medium from the grain. The corn remained on the screen and the medium was retained in a box made of 25 mm thick plywood.

3.2.2 Experimental design

In order to maintain a reasonably uniform initial medium temperature for every temperature level, the oven for heating the medium was set at a predetermined temperature and all observations were made. The oven was then reset for a different temperature level and the study continued. Therefore, in the design of the experiment, temperature levels were the main plots of a factorial experiment in a split-plot arrangement. The combination of four drying media, three residence times and three medium-to-grain mass ratios were sub-plots within the main plot units (Table 3.1), which resulted in 108 treatments. The residence times were different for each medium temperature: for 250°C 1, 2 and 3 min; for 200°C 1.5, 3 and 6 min; and for 150°C 2, 4 and 8 min. The response variable was the final moisture content, which was determined after a particular drying treatment. The drying experiment was replicated twice.



LEGEND

1) Fiberglass Insulation
2) Steel Cylinder Lined with Teflon
3) Thermocouples for Measuring Wet Bulb and Dry Bulb Temp
4) Data Logger
5) Corn
6) Wire Screen
7) Particulate Medium
8) Wooden Box
9) Variable Speed AC Motor
10) Clamp
11) Door
12) Door Hinge

Fig. 3.1 Schematic representation of the dryer

Table 3.1. Experimental factors and their levels

Factor	Indep. Variable		Levels 1	2	3	4
T	Medium temp. (°C)		150	200	250	-
M	Medium types		M1	M2	M3	M4
R	Medium-to-grain ratio		4	6	8	-
S	Residence time (min) at the media Temperature	150°C	2	4	8	-
		200°C	1.5	3	6	-
		250°C	1	2	3	-

3.2.3 Procedure

The grain used was yellow dent corn obtained from a farm near Montreal. The corn was harvested fresh, taken to the lab, sealed in plastic bags in approximately 750 g lots, and kept in a refrigerator at 2°C. At least 4 h before each experiment, the sealed bag was taken out of the refrigerator to equilibrate with the ambient temperature. Three samples were taken from the lot to determine the initial moisture content of the grain. ASAE standard S352.1 (ASAE, 1983) was followed for moisture content determination.

The media were heated at the required temperature for 6 h. The initial mass of corn for all treatments was 650 g. The corn was placed into the dryer and the medium was added. The door was closed and the motor was turned on. Optimum rotational speed of the cylinder was determined with a cylinder of the same size but with plexiglass ends (which facilitated observation of the mixing pattern) using the medium at room temperature. It was found that 20 r.p.m. was appropriate for adequate mixing of the grain and the medium, and this rotational speed was maintained throughout the experiment. At the beginning of each experiment, the ambient dry bulb and wet bulb temperatures were measured.

When the residence time was over, the dryer was stopped, the medium and the corn were separated. Samples of corn were taken for moisture content determination, and part of the grain was stored in a vacuum bottle to determine the temperature of the grain. The use of a hollow shaft for supporting the drum on one end facilitated the measurement of the dry bulb and wet bulb temperatures of the air inside the dryer during drying.

3.3 Results and Discussion

The results of this study indicate that molecular sieves are superior to sand for particulate medium drying. The highest moisture removed in percentage points (MRP) was 20.9 from an initial moisture content of 33.3 percent, wet basis (w.b.). This moisture loss was achieved as a result of using molecular sieve 4A (14-30) at 250°C for 3 minutes with MGMR of 8:1. For the same operating conditions, the MRP of sand was 11.7. The difference between the MRP of sand and molecular sieves was small at the lowest residence time but it increased with longer residence times. At the highest residence time, for all medium temperatures, the MRP of molecular sieves was almost twice that of sand.

The Statistical Analysis System (SAS) package (SAS Institute, 1985) was used to test the equality of means. The means of removed moisture percentage points (w.b.) are shown in Table 3.2. and the means of grain temperatures in Table 3.3. Although the means of removed moisture percentage points were different among different media, the MRP for sand was much lower than those of the molecular sieves. The molecular sieve 13X has wider diameters of pores than type 4A. Since the channel dimensions are among the factors affecting the kinetics of adsorption (Breck and Anderson, 1981), one would expect that molecular sieves 13X would produce the highest MRP. However, the data set shows that molecular sieves 4A (14-30 mesh) to be better for moisture removal. This could be attributed to the particle size distribution of 4A (14-30) which could result in a better contact between the drying medium and grain compared to 13X (8-12).

Table 3.2. Means of removed moisture in percentage points

Grouping *	Means	No. of Obs.	Medium
A	9.87	54	4A(14-30)
B	9.12	54	13X(8-12)
C	8.51	54	4A(8-12)
D	5.89	54	Sand

* Means with the same letter are not significantly different at the 0.05 level.

Table 3.3. Means of the grain temperature using different media

Grouping *	Means	No. of Obs.	Medium
A	90.40	54	13X(8-12)
A	89.20	54	4A(14-30)
A	88.85	54	4A(8-12)
B	74.13	54	Sand

* Means with the same letter are not significantly different at 0.05 level.

Figures 3.2 - 3.4 show MRP vs MGMR curves at different temperatures and residence times for the molecular sieves 13X(8-12) and sand. Similar results for the molecular sieves 4A(8-12) are given in Appendix A.

An analysis of the main effects of the factors studied is given in Table 3.4. It can be seen that the main effects of temperature (T), medium-to-grain mass ratio (R), medium type (M), and residence time (S) are significant at the 0.01 level. The two-way interactions, except for MxR, are significant at the 0.01 level. None of the three-way and four-way interactions are significant even at 0.1 level.

The relative humidity of the air in the dryer is a limiting factor to the diffusion of moisture from the grain surface to the air. The relative humidity (RH) was determined by measuring the dry bulb and wet bulb temperatures of the air in the dryer. The psychrometer was calibrated with a standard sling type psychrometer. In the observations made, the RH in the first 0.5 min varied and did not show a definite trend. Later it did stabilize and showed an increasing trend for sand (Fig. 3.5), while RH of the air in the drum dropped and remained steady for the molecular sieves. The rate of increase of RH depended on the sand temperature and sand-to-grain mass ratio, but it always passed 90 percent in less than 2 min. For the molecular sieves, RH lowered to a steady value of 10 - 20 percent.

The means of grain temperature after separation from the medium (Table 3.3) show that the mean grain temperature in the experiments using the molecular sieves do not significantly differ from one another, but the mean grain temperature using sand is significantly lower than those achieved using the molecular sieves. From this analysis, one can conclude that molecular sieves are better than sand as a medium for drying grain, due not only to their mass transfer properties but also to their heat transfer properties.

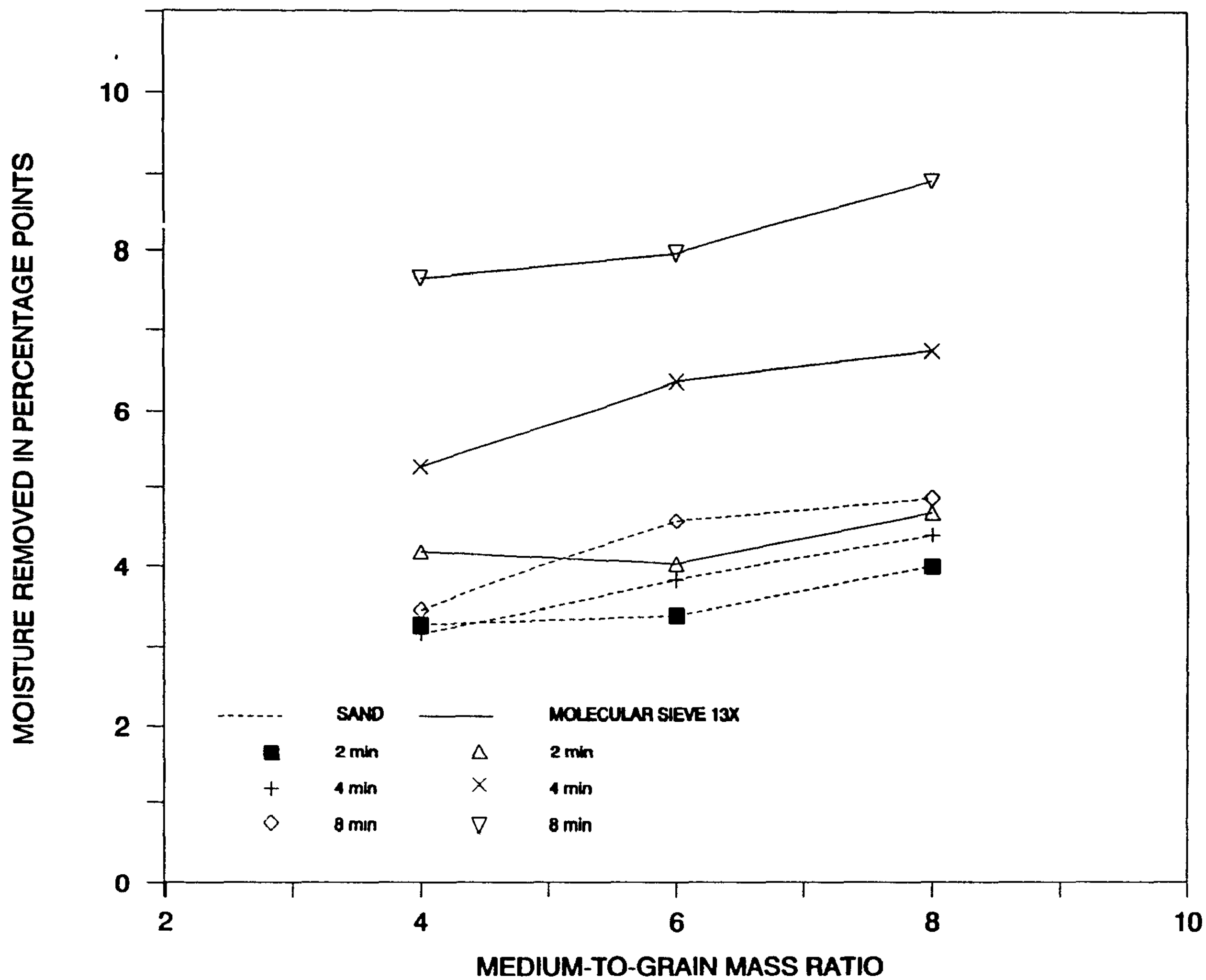


Fig. 3.2 Moisture removed with media at initial temperature of 150 C

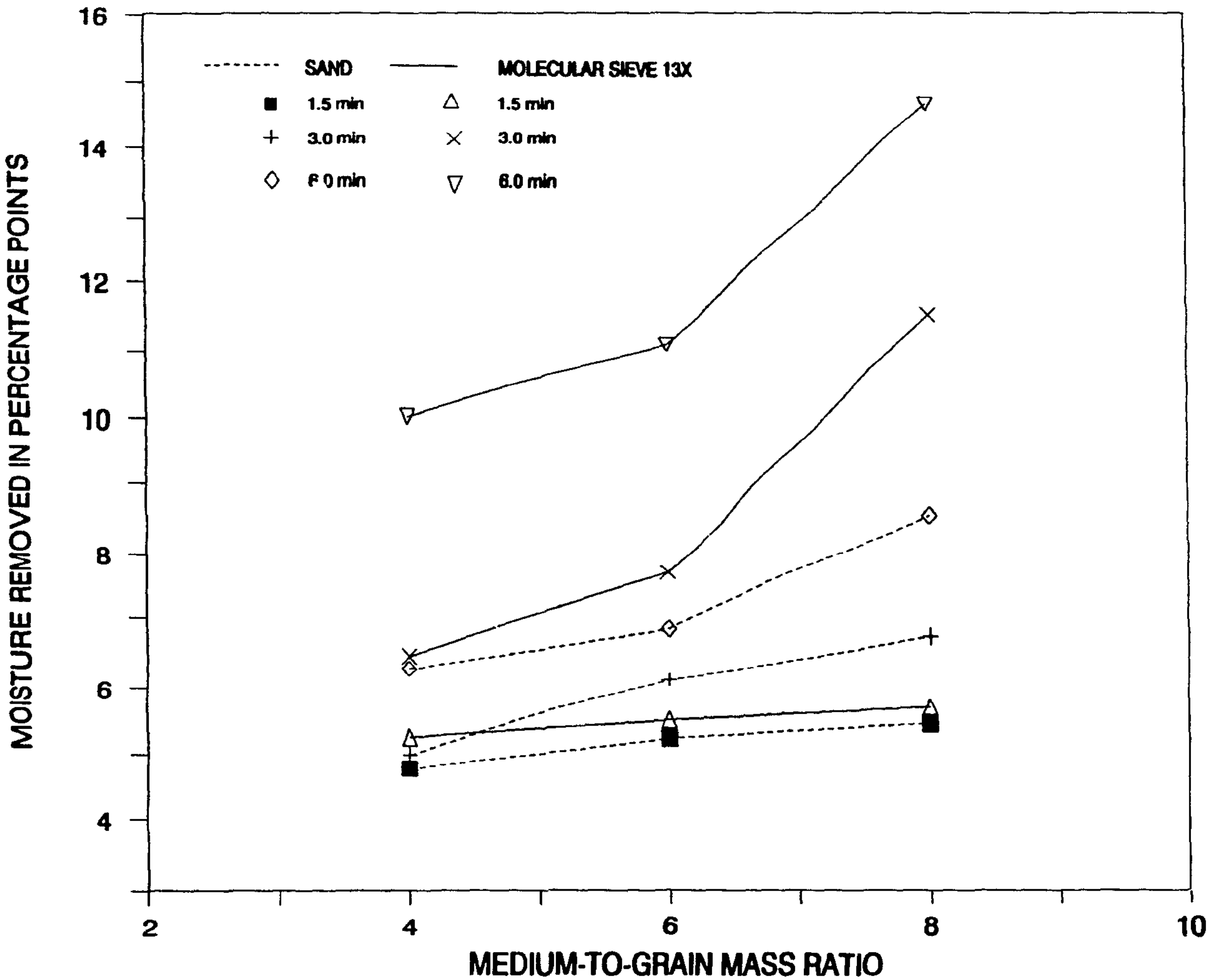
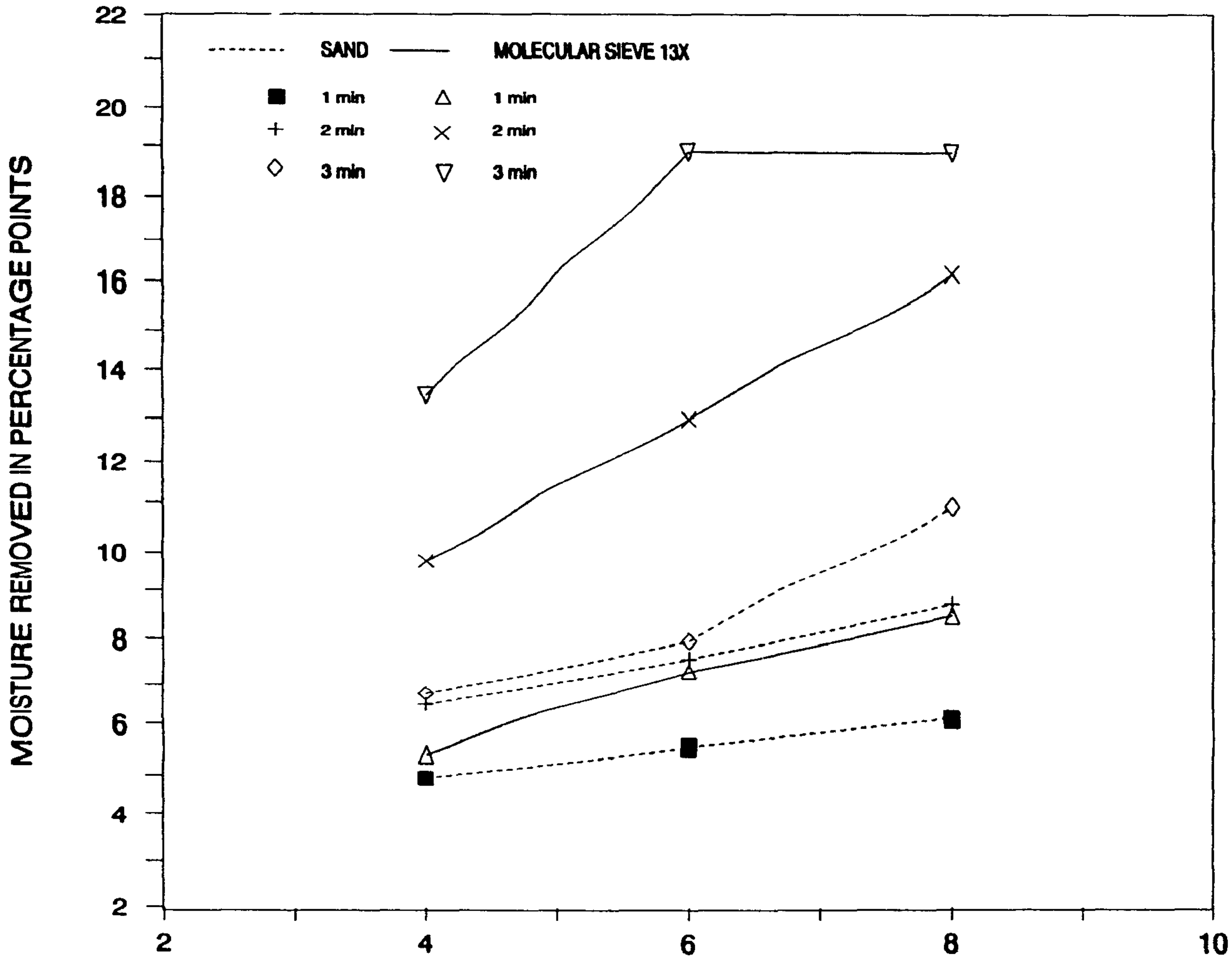


Fig. 3.3 Moisture removed with media at initial temperature of 200 C



MEDIUM-TO-GRAIN MASS RATIO
Fig. 3.4 Moisture removed with media at initial temperatures of 250 C

Table 3.4. Analysis of variance procedure and the interaction of main effect means

Dependent Variable: Moisture Content

Source	DF	Sum of Sq.	Means Sq.	F value	Prob > F
Model	110	3281.2110	29.8292	21.82	0.0001
Error	105	143.5435	1.3671		
Correc. Total	215	3424.7544			

Source	DF	ANOVA SS	F Value	Prob > F
T	2	1039.8322	1546.43	0.0006
M	3	483.5293	117.90	0.0001
T x M	6	91.4737	11.15	0.0001
S	2	895.9163	327.67	0.0001
MxS	6	128.8561	29.69	0.0001
TxMxS	12	23.6971	1.44	0.1577
R	2	260.2010	95.17	0.0001
TxR	4	78.6923	14.39	0.0001
MxR	6	11.7023	1.43	0.2113
SxR	4	26.6406	4.87	0.0012
TxMxR	12	20.4150	1.24	0.2633
MxSxR	12	17.2876	1.05	0.4066
TxSxR	8	10.8482	0.99	0.4467
TxMxSxR	24	29.0069	0.88	0.6221

T: medium temperature

M: medium type

R: medium-to-grain mass ratio

S: residence time

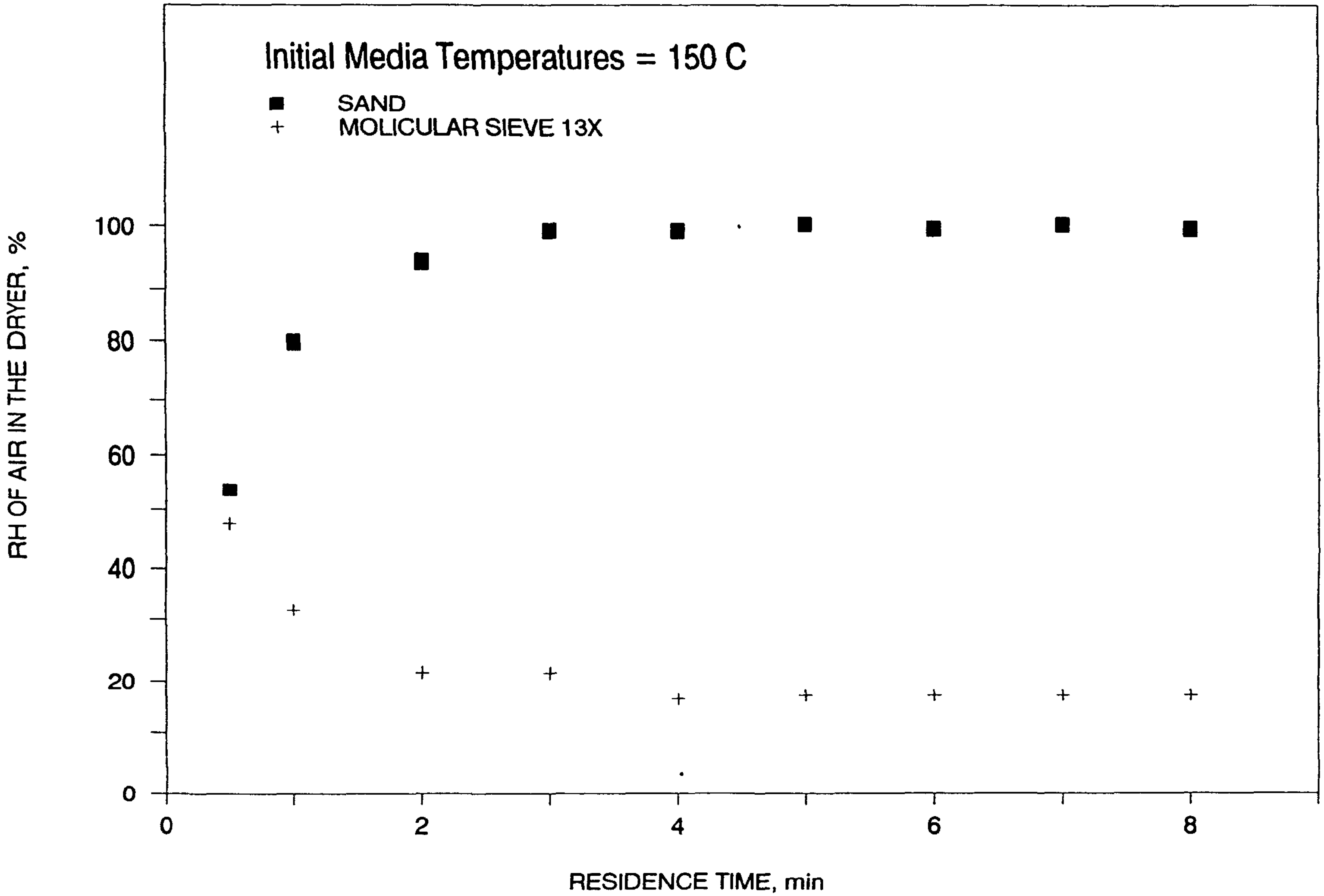


Fig. 3.5 Typical RH of air in the dryer

With regard to the regeneration of zeolite and its potential for drying the results of this study were positive. However, for practical purposes, one would not expect regeneration to take place in an electric oven but rather in a dryer, such as that described by Pannu and Raghavan (1987). This means that the residence time in the heating chamber would be much shorter while exposed to a higher temperature. Therefore, a model regeneration unit was constructed (Fig. 3.6) which employed the same burner used in the dryer of Pannu and Raghavan (1987).

It was observed that an exposure time of only about 2 min was sufficient for the medium to reach a temperature of 150°C. The heated medium was then mixed with moist corn following the methodology of section 3.2.

Results of these drying studies are presented in Fig. 3.7. For comparison, results of drying with the same type of zeolite regenerated in a convection type electric oven for 6 h are also presented. While the moisture removed is invariably higher for regeneration in the oven, for practical purposes the difference does not appear to be considerable. At the beginning of these studies it was not sure that the exposure of zeolite to the flame would damage the structure of the material irreversibly. There were no visible signs of change in the physical properties of the zeolite after exposure to the flame, no change of color or shape. The results of this part of the study led us to believe that for a real life situation, it is possible to use zeolite as a medium for heat and mass transfer in the prototype dryer.

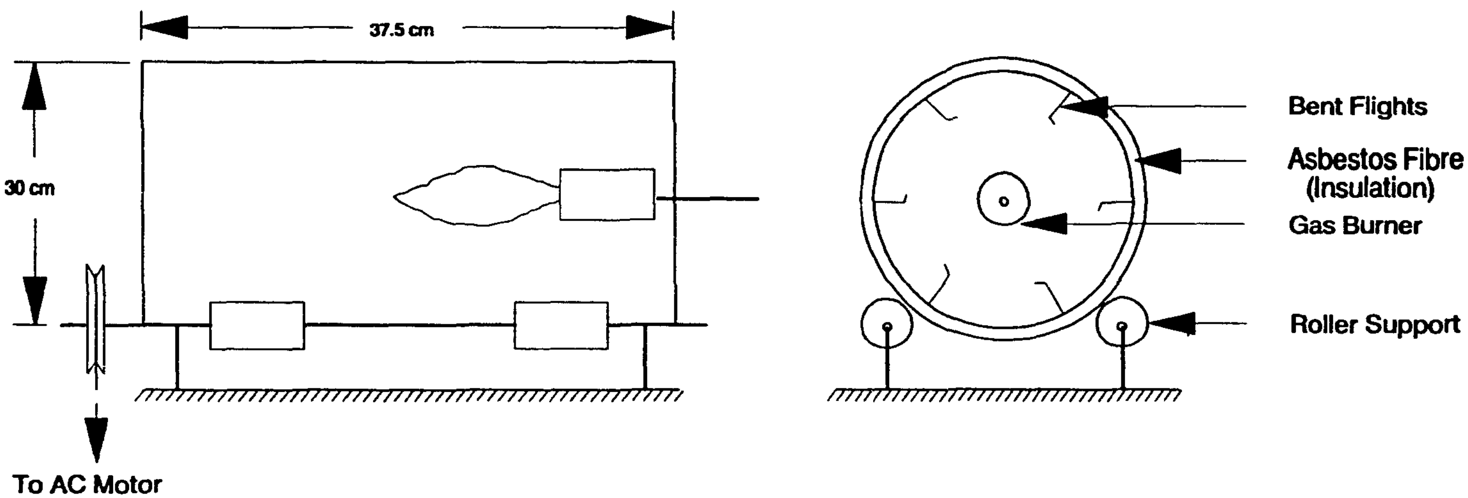


Fig. 3.6 Schematic diagram of the model regenerator

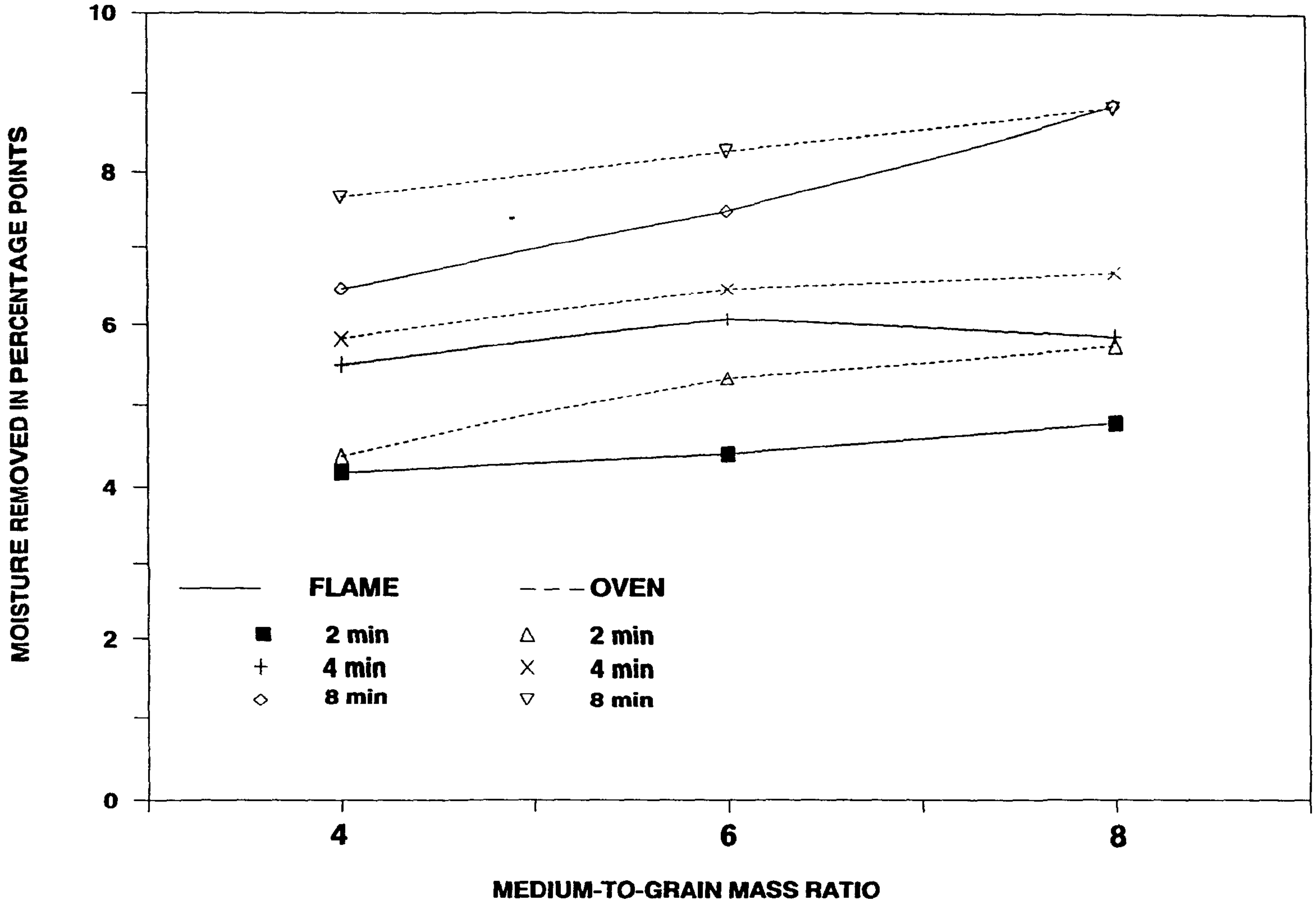


Fig 3.7 Results of drying corn with zeolites regenerated by different methods

3.4 Summary and conclusions

The potential of synthetic zeolites 4A and 13X as a granular medium for heating and drying corn was evaluated in a batch type dryer. The results of drying experiments using zeolites were compared with those of sand, the most commonly used particulate medium.

Molecular sieves performed better than sand as the medium for drying corn. The means of grain temperature using the molecular sieves were significantly higher than those of sand. This could be attributed to a higher heat transfer coefficient between molecular sieves and grain than between sand and grain.

The relative humidity of the air in the dryer when using sand approached saturation rapidly (> 90 % for times less than 2 min). The RH using molecular sieves dropped with residence time to reach a steady value of 10 - 20 percent.

With increased residence times, the difference between the MRP by the molecular sieves and sand increased. The mean MRP for the molecular sieves at the highest residence time, for all media temperatures, was about twice that achieved by sand.

CHAPTER FOUR

HEAT TRANSFER ASPECTS OF THE PROCESS

Steam is no stronger now than it was a hundred years ago,
but it is put to a better use — *Ralph Waldo Emmerson (1803 - 1882)*

Heat transfer is an important unit operation in food process engineering because almost all processed foods require some degree of heat transfer during the process. Researchers in the past two decades have focused on enhanced methods of heat transfer. Bergles (1978) remarked that interest in enhanced heat transfer has developed to a stage where it can be considered a major specialty in heat transfer research. One area in food process engineering in which enhanced heat transfer can be applied is the use of particulate medium for drying cereal grains.

In Chapter Three results, of drying studies in terms of the potential of molecular sieves for drying corn was reported. It was concluded that molecular sieves performed better than sand. In this chapter, analytical and numerical solutions of the differential equations of heat transfer for corn immersed in a heated bed of granular zeolite will be presented.

4.1 Analysis of the heat transfer process

4.1.1 Basic assumptions

The analysis of heat transfer process in this study is based on phenomenological laws: Fourier's law of heat conduction and the law of conservation of energy. In order to obtain an analytical or numerical solution of the differential equations describing heat transfer during grain drying by immersion in heated bed of granular zeolite the following assumptions are made:

1. The laws of continuum mechanics are applied to the system.

2. Thermal properties of the media are not temperature-dependent and will remain constant throughout the process.

3. Each corn kernel is completely surrounded by the heating medium.

4. The volumetric heat capacity of the air layer is negligible compared to that of the solid medium; the energy transferred in heating the air is negligible.

5. The heat of adsorption on zeolite is the same order of magnitude as the heat of vaporization of moisture from corn.

6. All heat lost by the heating medium is utilized to raise the sensible heat of the grain.

4.1.2 Heat transfer models for the corn-zeolite mixture

Schlünder (1981) stated that the particular heat transfer fundamentals for the process of heat transfer between a submerged surface and a bed of granular material is clear today. He described that heat transfer from a submerged surface to a bed of particles takes place in two steps: i) heat transferred from a submerged surface onto the surface of the gas layer adjacent to the particle, and ii) heat transfer by conduction within each particle of the bed. Therefore the conceptualization of the process will involve that of heat transfer by conduction within the granular medium and in the corn kernel but combined convective and conductive heat transfer between the two surfaces.

We will consider two models. In the first model it is assumed that an adiabatic heat transfer between the heating medium (heated granular zeolite) and the medium being heated (corn kernel) takes place. It is also assumed that there exists a temperature gradient between the outer boundary of the heating medium surrounding the kernel and the centre of the kernel (Fig. 4.1). An overall thermal contact resistance between the particles of the heating medium and the medium being heated is included. The mathematical model and the boundary conditions can be stated as:

$t > 0$

$$\frac{\partial T_c}{\partial t} = \alpha_c \left(\frac{2}{R}\frac{\partial T_c}{\partial R} + \frac{\partial^2 T_c}{\partial R^2}\right), \qquad 0 \le R \le R_1$$

$$\frac{\partial T_z}{\partial t} = \alpha_z \left(\frac{2}{R}\frac{\partial T_z}{\partial R} + \frac{\partial^2 T_z}{\partial R^2}\right), \qquad R_1 < R \le R_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (4.1)$$

Initial conditions ($t = 0$)

$T_c\ (R,0) = T_{ci}$ $\qquad 0 \le R \le R_1$

$T_z\ (R,0) = T_{zi}$ $\qquad R_1 < R \le R_2$

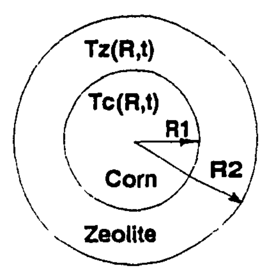


Fig. 4.1 Nomenclature for the first heat transfer model

Boundary conditions

$t > 0$

$R = 0$ $\qquad \dfrac{\partial T_c}{\partial R} = 0,$

$R = R_1$ $\qquad -\lambda_c \dfrac{\partial T_c}{\partial R} = h\,(T_c - T_z)$

$R = R_2$ $\qquad \partial T_z/\partial R = 0$

The second model, which is also for adiabatic heat transfer, assumes that the temperature of all the granular material surrounding the corn kernel is the same at any time. This assumption suggests that there is no heat transfer between the particles of the heating medium. Therefore, by taking into account the total mass of the heating medium, the model is basically that of heat transfer between a single particle of the heating medium and the particle being heated (Fig. 4.2). Mathematically this model can be formulated as:

$t > 0 \qquad 0 \le R \le R_1$

$$\frac{\partial T_c}{\partial t} = \alpha_c \left(\frac{2}{R}\frac{\partial T_c}{\partial R} + \frac{\partial^2 T_c}{\partial R^2}\right), \quad \text{..........} \ (4.2\ a)$$

$t > 0 \qquad 0 \le r \le r_o$

$$\frac{\partial T_z}{\partial t} = \alpha_z \left(\frac{2}{r}\frac{\partial T_z}{\partial r} + \frac{\partial^2 T_z}{\partial r^2}\right), \quad \text{..........} \ (4.2\ b)$$

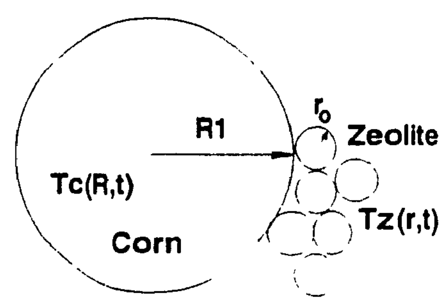


Fig. 4.2 Nomenclature for the second heat transfer model

$$\frac{\partial T_c}{\partial R} = \frac{\alpha_c}{\lambda_c}(T_A - T_c) \qquad R = R_1$$

$$\frac{\partial T_z}{\partial r} = \frac{\alpha_z}{\lambda_z}(T_A - T_z) \qquad r = r_o$$

$$\frac{\partial T_c}{\partial R} = 0 \quad \text{for} \quad R=0, \qquad \text{and} \qquad \frac{\partial T_z}{\partial r} = 0 \quad \text{for} \quad r=0$$

$$T_{eq} = \frac{p\, C_{pz}\, T_{zi} + C_{pc}\, T_{ci}}{p\, C_{pz} + C_{pc}} \qquad T_A = \frac{r_o\, \phi_z\, \alpha_c\, T_c + p\, R_o\, \phi_c\, \alpha_z\, T_z}{r_o\, \phi_z\, \alpha_c + p\, R_o\, \lambda_c\, \phi_c}$$

$$T_c\,(R,0) = T_{ci} \qquad T_z\,(r,0) = T_{zi} \qquad T_c\,(R,\infty) = T_z\,(r,\infty) = T_{eq}$$

4.1.3 Residence time

The residence time for heat and mass transfer between the heating medium and the medium being heated is an important parameter. Schlünder (1981) remarked that reliable description of particle motion in agitated beds and/or fluidized beds is still a problem. The flow pattern in a rotary cylinder has been studied by several researchers. It is believed that in a rotating cylinder, the speed of the drum and its diameter are among the most important parameters affecting the mixing of the particles. For each medium there is a critical speed of rotation, N_c.

It can be said that with varying cylinder diameter, dynamic similarity is supposed to exist at equal Froude numbers. At N_c, the Froude number (Fr) is 1.0. centrifuging starts and particles are taken along the moving wall (Rutgers, 1965). This stage is also referred to as the equilibrium state (Clump, 1967). Below the critical point, several types of particle movement can be expected. For Fr in the range of 0.55 - 1, depending on the granular material and the cylinder wall characteristics, parts of the material are showered to the bottom of the cylinder (Fig. 4.3), in a movement called cataracting. At lower speeds, cascading and rolling take place.

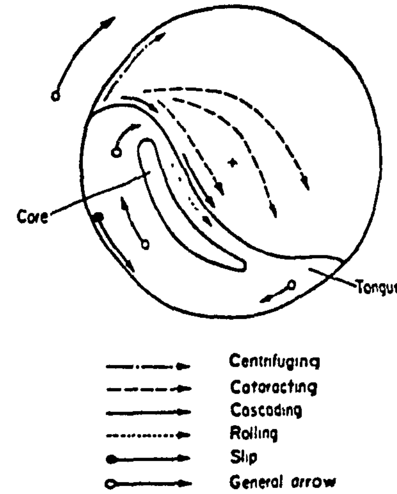


Fig 4.3 Types of particle movement in rotating cylinder (*from* Rutgers, 1965)

Clump (1967) stated that the following relationship for the cylinder speed and its diameter holds:

$$N = \frac{C}{d^{0.47}\ V^{0.14}} \qquad \text{.....................} \qquad (4.3)$$

where

N - rpm

C - a constant

d - inside diameter of the cylinder

V - volume of the cylinder occupied by solids (%)

Clump (1967) also mentioned that best mixing takes place when the particle movement is between cataract and equilibrium. A few mixing experiments using cold zeolite and grain corn were carried out. Observations indicated that operating in the cascading state resulted in adequate mixing of the two media.

It goes without saying that in this type of drying it is not favorable to separate the particles in contact and operate in the cataracting state. In the cascading state, especially if a high mass ratio of the heating medium to grain is used, the grain will be enclosed in the medium at all times during the process. Therefore, the problem of determining the residence time will be appreciably simplified . The contact time will be the residence time, the period when the two media are kept in the cylinder.

4.2 Heat Transfer Parameters

4.2.1 <u>Thermal conductivity</u>

The thermal properties of corn and other cereal grains have been well documented. The thermal conductivity of corn was taken from the data published by the American Society of Agricultural Engineers, ASAE standard D243.2 (ASAE, 1983). The effective thermal conductivity of zeolite was calculated using the following relation (Dietz, 1979):

$$\frac{\lambda_{eff}}{\lambda_A} = 1.14 \left(\frac{\lambda_s}{\lambda_A}\right)^{1/2} \frac{K_0 \left[(40 \lambda_A/\lambda_s)^{1/2}\right]}{K_1 \left[(40 \lambda_A/\lambda_s)^{1/2}\right]} \qquad \text{..................} \quad (2.4)$$

The effective thermal conductivity of zeolite particles was also experimentally determined in the laboratory. A schematic diagram of the equipment is given in Appendix B.

4.2.2 Heat capacity

Like thermal conductivity, the heat capacity of corn was taken from the above-mentioned ASAE standard, and the heat capacity of zeolite was determined experimentally in the laboratory by differential scanning calorimetry. A model DSC7 Differential Scanning Calorimeter with a TAC7 Instrument Controller interface was connected to a Perkin-Elmer 7700 Professional Computer. Details of the theory and procedure (basically a continuous measurement of heat flow rate and rate of change of temperature: $dH/dt = m\, C_p\, dT/dt$) is given by O'Neill (1966).

4.2.3 Heat transfer coefficient

The heat transfer coefficient was determined by the following model for Nu, as suggested by Downs et al. (1977):

$$Nu = C_o\, (X_1)^{C1}\ (X_2)^{C2}\ \dots\ (X_n)^{Cn} \qquad \text{..................} \quad (2.10)$$

where C_o is the coefficient and C_n are the exponents of the n dimensionless terms (X_n). Sibley and Raghavan (1986) experimentally determined the significant terms for heat transfer in a mixture of sand and grain corn. The dimensionless terms of significance were: Fourier number (Fo), the medium-to-grain mass ratio (MGMR), and the temperature ratio $(T_{m,i} - T_{g,i})/T_{m,i}$. Based on the values of the coefficients of the dimensionless terms reported by Sibley and Raghavan (1986), the following expression for Nu can be written:

$$Nu = 2.4899(Fo)^{-0.4076} (MGMR)^{0.3769} ((T_{m,i} - T_{g,i})/T_{m,i})^{1.4357} \quad \text{..................} \quad (2.11)$$

Using the above expression, the value of the heat transfer coefficient between the granular zeolite and the grain corn was found to be in the range of 50 - 312 $W/m^2{\cdot}K$.

4.3 Experimental scheme

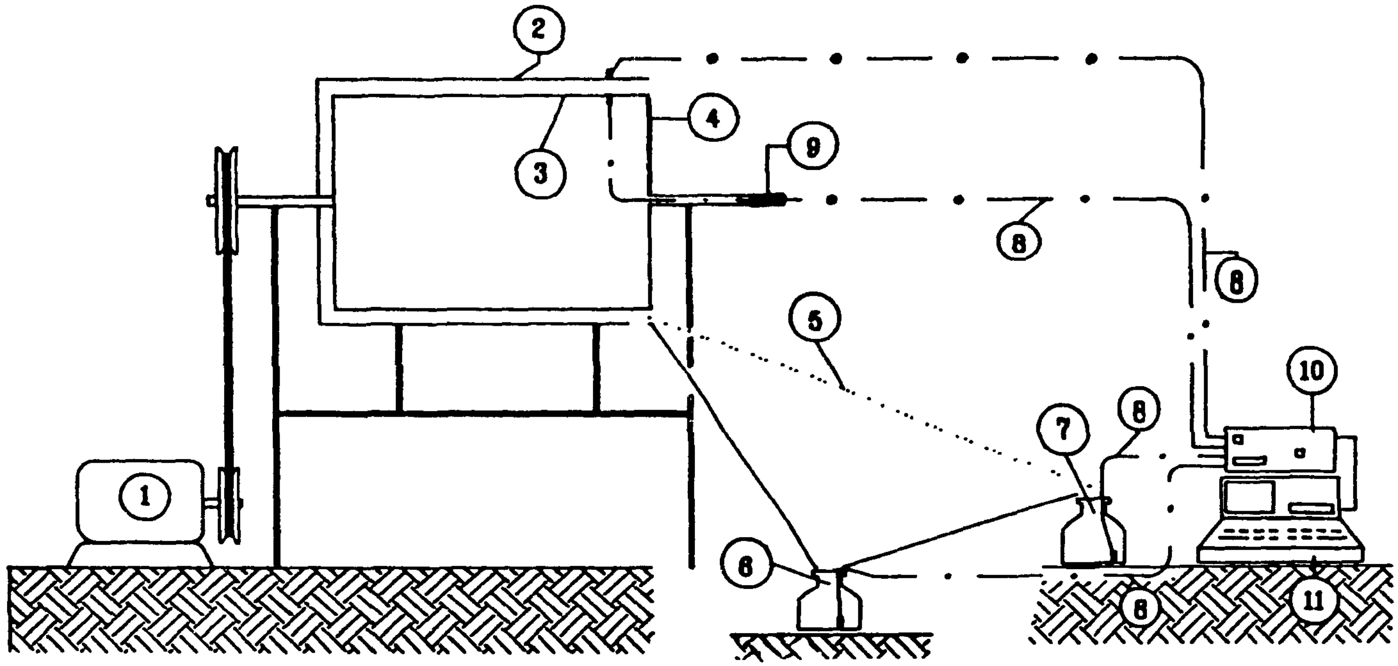
The heating medium was natural zeolite (chabazite). The initial medium temperatures were 140, 160, 180, 200, and 220°C. The medium was heated by placing it in enamelled trays and keeping it in an electric oven overnight at the set temperature.

The material to be heated was naturally moist yellow dent corn. The mass of corn for each experiment was 0.5 kg. Experiments were conducted to determine the average volume (and thus the radius) of corn kernels by a pycnometer, with toluene ($C_6H_5CH_3$) as the fluid. Details of the method are given by Mohsenin (1986). The average radius of 10 kernels was found to be 0.412 cm. A medium-to-grain mass ratio of 3:1 was used.

The grain and zeolite were mixed in a rotating cylinder. In order to avoid heat loss to the cylinder and the ambient environment, the cylinder was rotating inside another cylinder (stationary) which was covered with heating mats. Thermocouples connected to a data acquisition and control unit were placed to determine the surface temperature of the inner cylinder and the outside surface temperature of the outer cylinder. The temperatures were measured continuously, and when the temperature of the outside cylinder was lower than the inside cylinder, the heaters were switched on.

The cylinders were made of steel. The inner diameter of the rotating cylinder was 27 cm, the wall thickness 0.3 cm and the length 30 cm. The cylinders were machined such that the gap would not be much more than that required for free rotation. A schematic representation of the experimental set up is given in Fig. 4.4.

At the beginning of each experiment, the cylinder temperature (inside and outside) was brought to 70°C, the grain and the heating medium were added and the cylinder door was closed. The cylinder was rotated by an AC motor at 20 rpm. When residence time was over, the motor was switched off and the contents of the cylinder were separated by means of a wire screen. The grain and the medium were collected in separate vacuum flasks and their temperatures recorded. Observed values of corn and zeolite surface temperatures after mixing (T_{zi} = 140, 180 and 220°C) are presented with the numerical solutions (Section 4.5). The results for the mixtures with initial zeolite temperatures of 160 and 200°C are given in Appendix C.



LEGEND

1	AC MOTOR	7	THERMOS FOR COLLECTING CORN
2	EXTERIOR (STATIONARY) CYLINDER	8	THERMOCOUPLES
3	INTERIOR (ROTATING) CYLINDER	9	SLIP RING
4	DOOR FOR LOADING AND UNLOADING CHARGE	10	DATA AQUISITION & CONTROL UNIT
5	WIRE SCREEN	11	COMPUTER
6	THERMOS FOR COLLECTING ZEOLITE		

Fig. 4.4 Schematic diagram of the adiabatic dryer

4.4 Analytical solution

For the first model an analytical solution is given by Luikov (1968). However, the mathematical model employs a perfect thermal contact at the interface. Mathematically speaking:

$$T_c = T_z \qquad \text{for } R = R_1 \qquad \text{and} \qquad t > 0$$

The solution given is as follows:

$$\frac{T_c\,(R,t)}{T_{ci}} = \frac{2\,R_2}{R} \sum \frac{1}{\psi(\mu_n)} \sin \mu_n \frac{R}{R_1} \sin \mu_n\,(\alpha_c/\alpha_z)^{1/2} \text{ x } (R_2/R_1 - 1) \exp(-\mu_n^2\,Fo_c) \qquad \text{.................... (4.4 - a)}$$

$$\frac{T_z\,(R,t)}{T_{zi}} = \frac{2\,R_2}{R} \sum \frac{\sin^2 \mu_n}{\psi(\mu_n)} \sin\,(\alpha_c/\alpha_z)^{1/2}\left(\frac{R_2 - R}{R_1}\right) \exp(-\mu_n^2\,Fo_z) \qquad \text{.................... (4.4 - b)}$$

$$\text{where} \quad \psi(\mu_n) = \frac{\lambda_c}{\lambda_z} (\lambda_c/\lambda_z)^{1/2}\,\mu_n \sin^2 (\alpha_c/\lambda_z)^{1/2}\,\mu_n(R_2/R_1 - 1) + (\alpha_c/\alpha_z)^2\,(R_2/R_1 - 1\,)$$

$$\text{x}\mu_n \sin^2 \mu_n + \frac{1 - (\lambda_c/\lambda_z)}{(\lambda_c/\lambda_z)^{1/2}\,\mu_n} \text{ x } \sin^2 \mu_n \sin^2 (\alpha_c/\alpha_z)^{1/2}\,(R_2/R_1 - 1)\,\mu_n$$

$$\text{and} \qquad Fo_c = \alpha_c\,t/R_1^2, \qquad Fo_z = \alpha_z\,t/R_2^2$$

As stated by Carslaw and Jaeger (1959), the assumption of perfect contact is valid only when contact between the surfaces is very intimate, e.g. welded or soldered surfaces. For other cases, where there are finite contact resistances between the two media, the rates of heat transfer are proportional to the temperature differences for the two media surfaces.

The heat transfer process in the second model considers a uniform temperature for all particles of the heating medium. It is further assumed that heat is transferred from the heating medium (small spheres, in this case) to the air layer and from there to the surface of the inner sphere (Fig. 4.2). To solve the system of differential equations (Eqns. 4.2), it must be realized that the system has time-dependent boundary conditions. The approach to be taken is a method of successive approximation. First, the problem is solved for the grain being heated using constant boundary conditions of the heating medium. From this approximate solution, the time-dependent relation for the surface temperature of the heating medium is obtained. The ultimate step is to use this time-dependent relation to determine a relation for the temperature of the material being heated. The mathematical procedure is basically the application of Duhamel's principle (Özisik, 1980).

The relation for the surface temperature of zeolite particles as described by Shabanov (1963) is:

$$\frac{T_z(r,t) - T_{eq}}{T_{zi} - T_{eq}} = \{L_1 - M_1 [L_1 - 1 + m_1 (\frac{L_2}{m_1 - m_2} + \frac{L_3}{m_1 - b_1} + \frac{L_4}{m_1 - b_2}) - M_2 \frac{L_1 m_1}{m_1 - m_2}]$$

$$L_1 M_1 t\} e^{-m1 t} + \{L_2 - M_2 [L_2 - 1 + m_2 (\frac{L_1}{m_1 - m_2} - \frac{L_3}{m_2 - b_1} - \frac{L_4}{m_2 - b_2})]$$

$$+ M_1 \frac{L_2 m_2}{m_1 - m_2} - M_2 L_2 m_2 t\} e^{-m2t} + L_3 \{1 + b_1 [\frac{M_1}{m_1 - b_1} + \frac{M_2}{m_2 - b_1}]\} e^{b1t}$$

$$+ L_4 \{1 + b_2 [\frac{M_1}{m_1 - b_2} + \frac{M_2}{m_2 - b_2}]\} e^{-b2t} \qquad \text{..................} \qquad (4.5)$$

where

$$L_1 = M_1 \left[1 - m_1 \left(\frac{B_1}{m_1 - b_2} + \frac{B_2}{m_1 - b_2}\right)\right],$$

$$L_2 = M_2 \left[1 - m_2 \left(\frac{B_1}{m_2 - b_1} + \frac{B_2}{m_2 - b_2}\right)\right],$$

$$L_3 = B_1 \left[b_1 \left(\frac{M_1}{m_1 - b_1} + \frac{M_2}{m_2 - b_1}\right) - \frac{C_{pz}}{pC_{pc}}\right]$$

$$L_4 = B_2 \left[b_2 \left(\frac{M_1}{m_1 - b_2} + \frac{M_2}{m_2 - b_2}\right) - \frac{C_{pz}}{pC_{pc}}\right]$$

$$M_1 = \frac{2Bi_z^*}{\eta_1^2 + (Bi_z^*)^2 - Bi_z^*},$$

$$M_2 = \frac{2Bi_z^*}{\eta_2^2 + (Bi_z^*)^2 - Bi_z^*},$$

$$B_1 = \frac{2Bi_c^*}{\mu_1^2 + (Bi_c^*)^2 - Bi_c^*},$$

$$B_2 = \frac{2Bi_c^*}{\mu_2^2 + (Bi_c^*)^2 - Bi_c^*},$$

Bi^* is a modified Bi defined as:

$$Bi_z^* = Bi_z \cdot \frac{1}{1 + \dfrac{R_o\ o_c\ \alpha_z}{p\ \alpha_c\ r_o\ o_z}}$$

$$Bi_c^* = Bi_c \cdot \frac{1}{1 + \dfrac{p\ r_o\ o_z\ \alpha_c}{\alpha_z\ R_o\ o_c}}$$

$m_1 = \eta_1^2\ \alpha_z/r_o^2$, $\qquad m_2 = \eta_2^2\ \alpha_z/r_o^2$,

$b_1 = \mu_1^2\ \alpha_c/R_o^2$, $\qquad b_2 = \mu_2^2\ \alpha_c/R_o^2$,

η_1, η_2, μ_1, and μ_2 are the first two roots of the transcendental equations

$$\tan \eta = - \frac{\eta}{Bi_z^* - 1}, \qquad \tan \mu = \frac{\mu}{Bi_c^* - 1}$$

4.5 Numerical solution

The analytical solutions were given in the previous section to provide an insight into the complexity of the solution of the heat transfer problem. A few points regarding these analytical solutions should be mentioned. Firstly, while the solutions are in the closed form they are far from exact solutions. These solutions require the use of several parameters, which are approximate values, such as roots of transcendental functions, and these parameters appear many times (in Eqn 4.5 more than a hundred times) in different arithmetic operations. Secondly, the mathematical model does not take into account the effect of surface contact on heat transfer. And, finally, the amount of arithmetic work involved should not be ignored. As remarked by Özisik (1968), numerical solutions of differential equations of heat transfer are sought for different reasons, such as complicated geometries or boundary conditions. Furthermore, numerical evaluation of the analytical solution sometimes becomes too laborious and the numerical solution using a digital computer then proves very practical.

The numerical method employed in this study is referred to as the Numerical Method of Lines (NMOL). This method which is basically a finite difference approximation is a powerful tool for solving time-dependent partial differential equations (PDEs). By discretizing the original spatial derivative(s), a semi-discrete approximating system of ordinary differential (ODEs) are produced. The solutions to these ODEs are sought through the established methods and thus an approximate solutions of the PDEs are obtained (Sincovec and Madsen, 1975). A flowchart of the use and structure of the computer programs is given in Appendix D.

The computer software employed in this study, which makes use of NMOL, is called Differential Systems Simulator, Version 2 (DSS/2). The source code for the

NMOL program to call the DSS/2 subroutines written in FORTRAN 77 is given in Appendix D.

Although numerous examples for comparing the numerical solution and the analytical solutions are provided by the developers of the DSS/2 (Schiesser, 1977), it is still interesting to compare the temperature profile based on the energy balance of the system as simulated by a computer program and the numerical solution of the governing heat transfer equations by NMOL. The result of the program written on the basis of energy balance (Schuepp, 1990) is shown in Fig. 4.6. It can be compared with the solution using NMOL given in Fig. 4.5. It should be pointed out that in Fig 4.5, the abscissa corresponds to the nodal points. While the corn radius and the thickness of the surrounding medium are not equal, they are both divided into the same number of nodal points. In Fig. 4.6, the abscissa is directly related to units of length and corresponds to the distance from the centre of the corn. The source code for the computer programs for a temperature profile based on energy conservation — written in BASIC computer language — is also given in Appendix D.

Figure 4.7 shows the temperature profile of the mixture with perfect contact at the interface. It can be seen that these values of corn surface temperature are much higher than the corresponding values shown in Fig. 4.5, where a finite contact resistance is considered. The grain temperatures predicted by the model are presented with the experimental values in Figs. 4.8 - 4.10. The theoretical grain temperatures obtained by NMOL are higher than the experimental values. It is hard to pinpoint whether the discrepancy between the predicted values and the observed values is due to the model or the experimental values. However, it is true that the lower values of the measured temperature could be attributed in part to (i) the method of temperature measurement

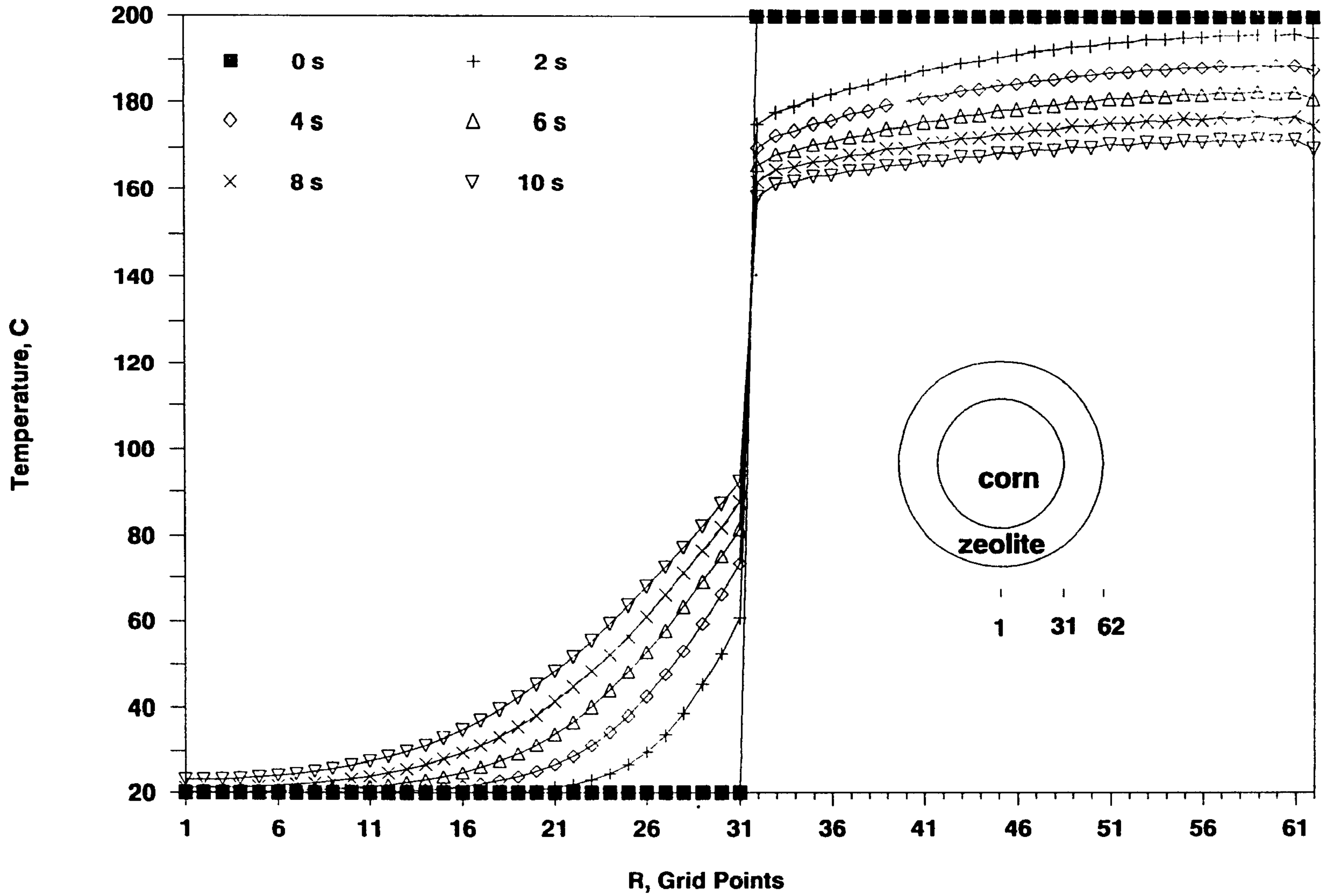


Fig 4.5 Temperature profile in a corn-zeolite mixture by NMOL

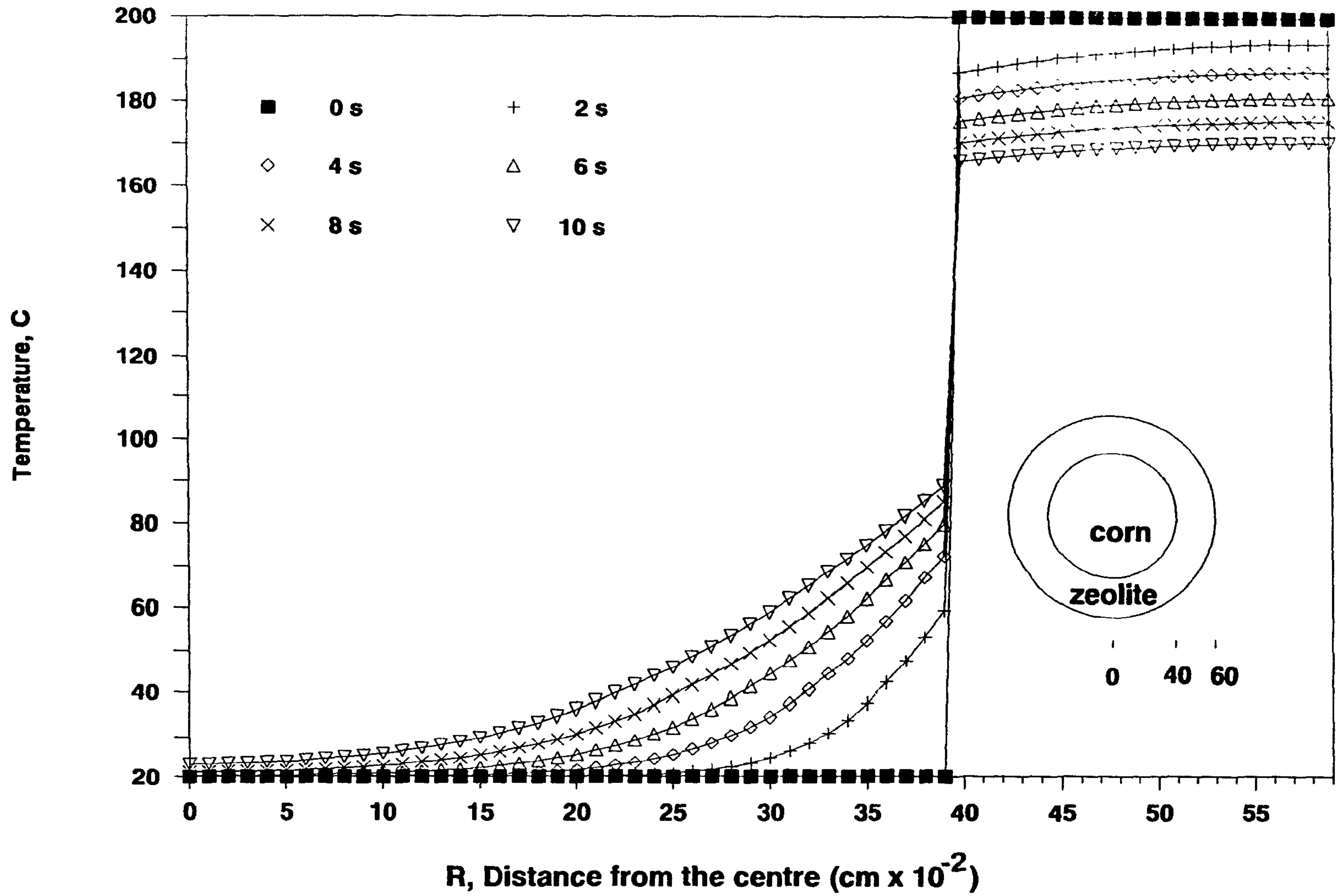


Fig 4.6 Temperature profile in the mixture based on energy balance

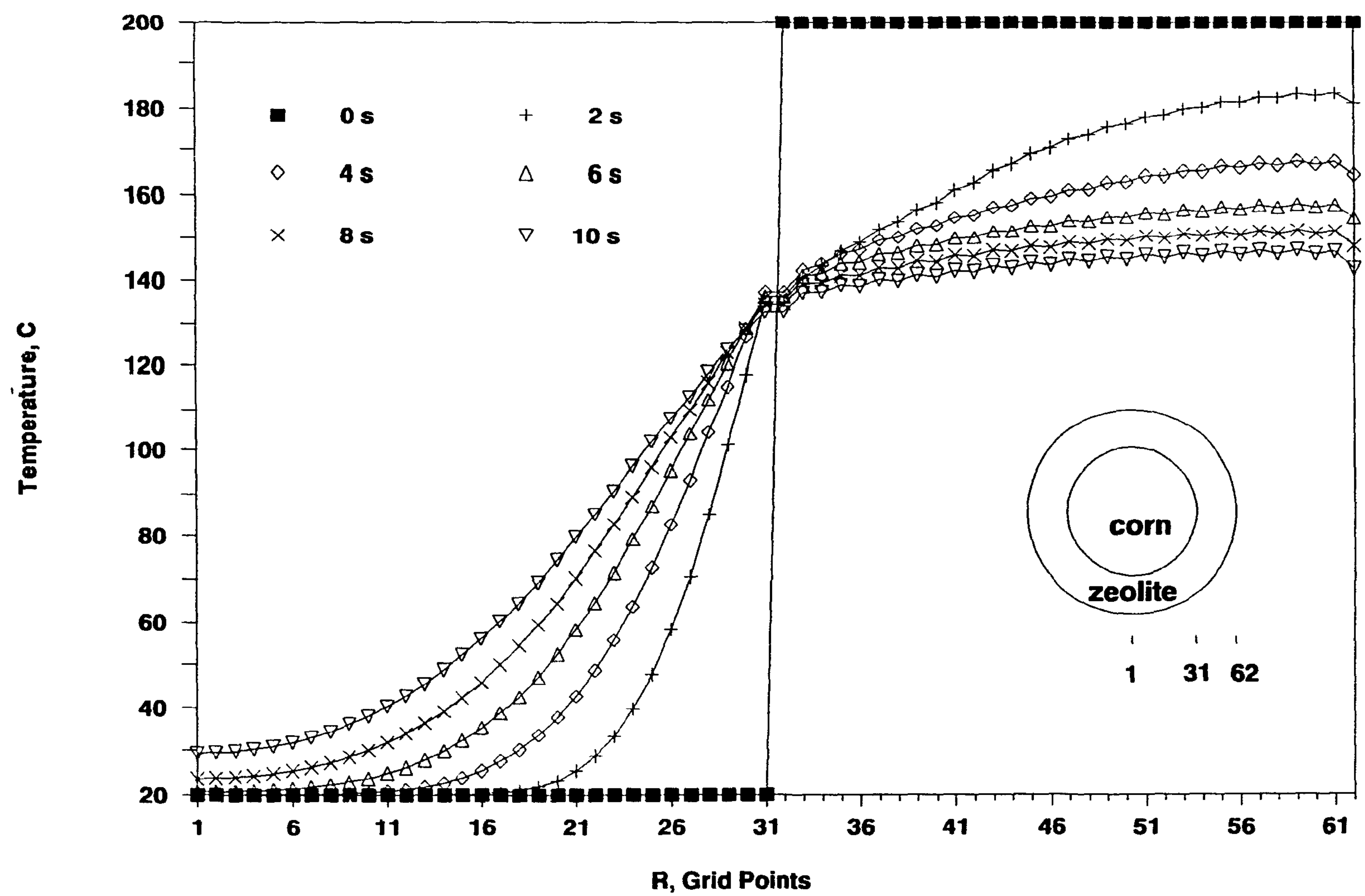


Fig 4.7 Temperature profile in the mixture with perfect thermal contact

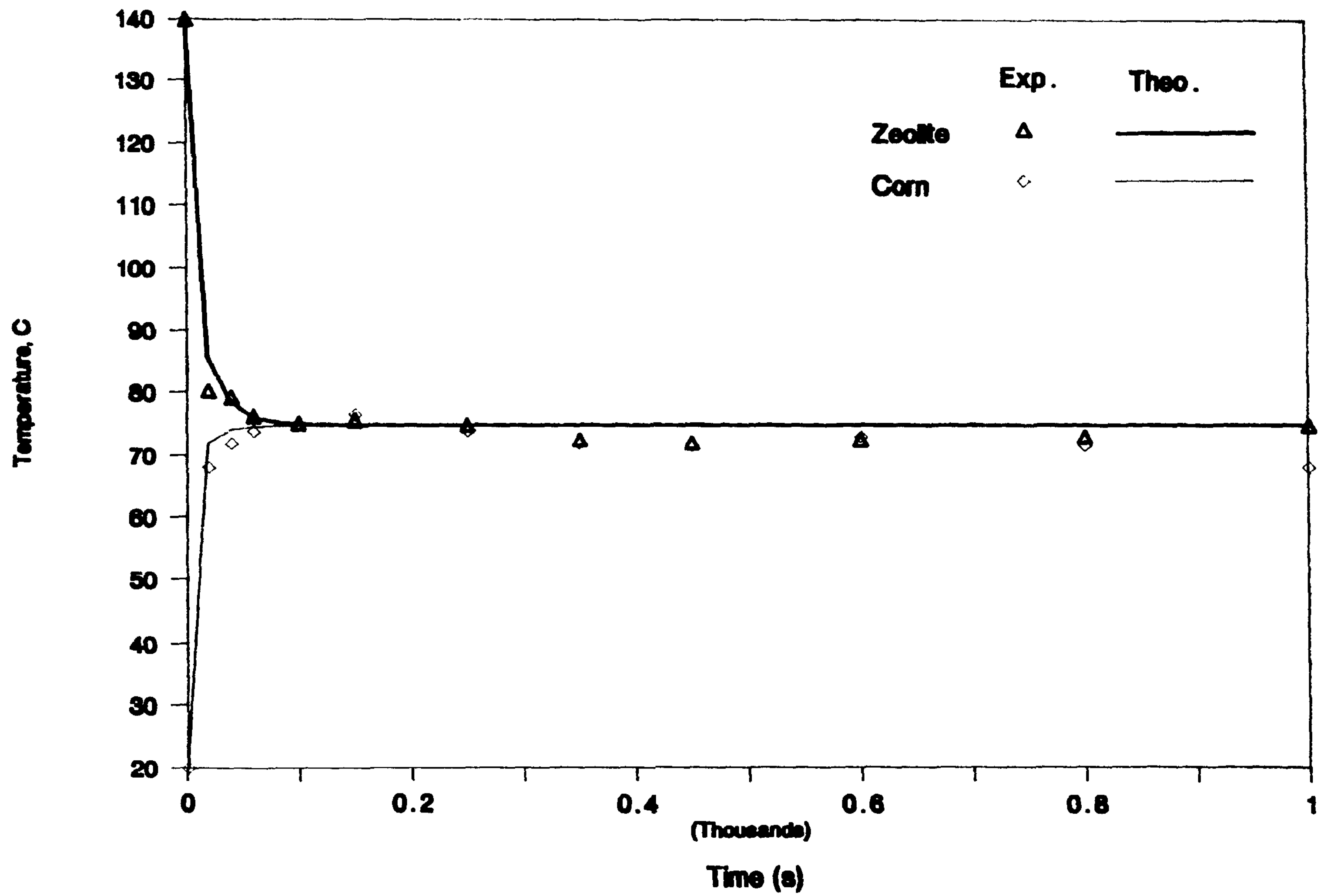


Fig 4.8 Theoretical and experimental values of corn and zeolite temperatures

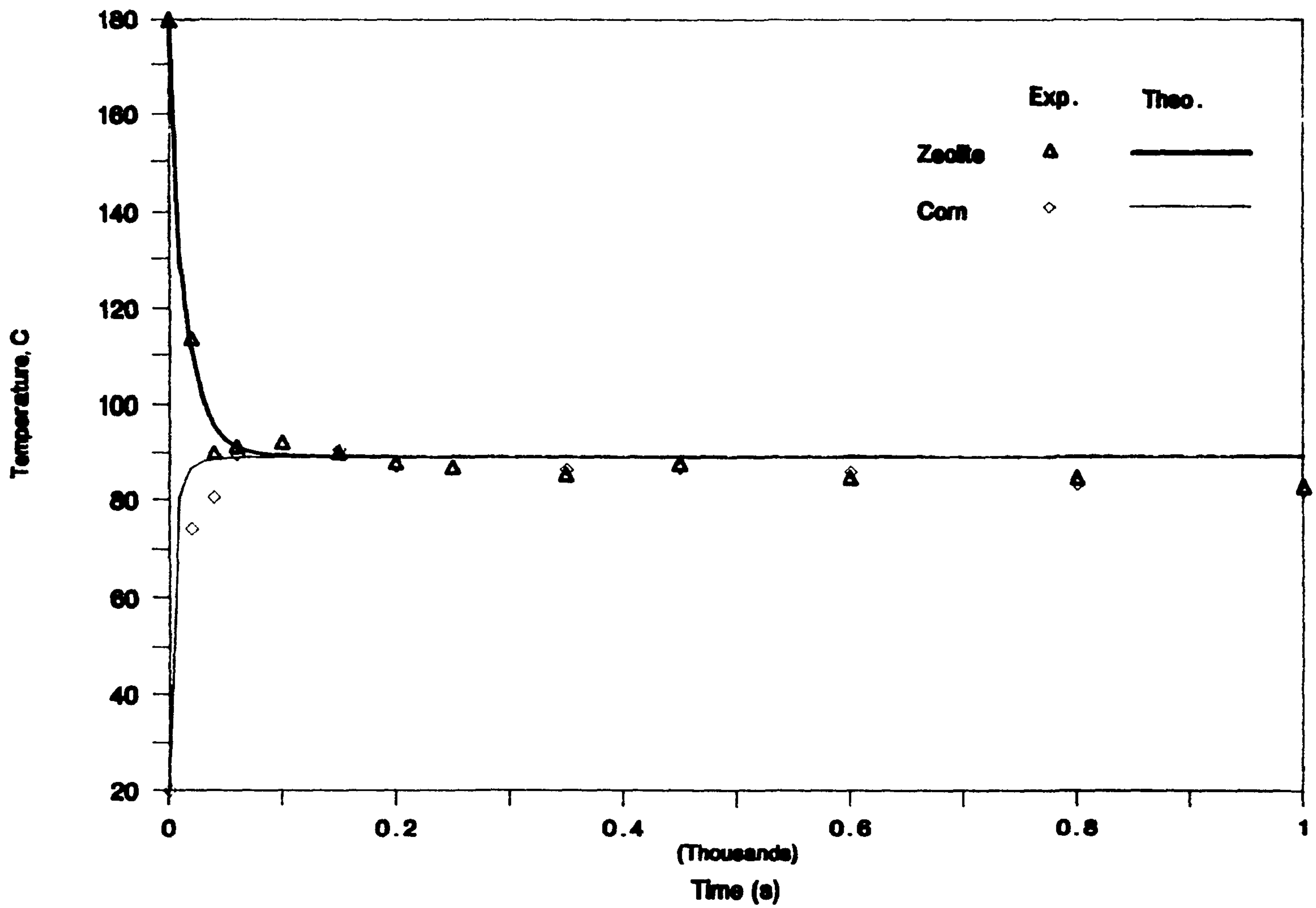


Fig 4.9 Corn and zeolite surface temperatures after mixing

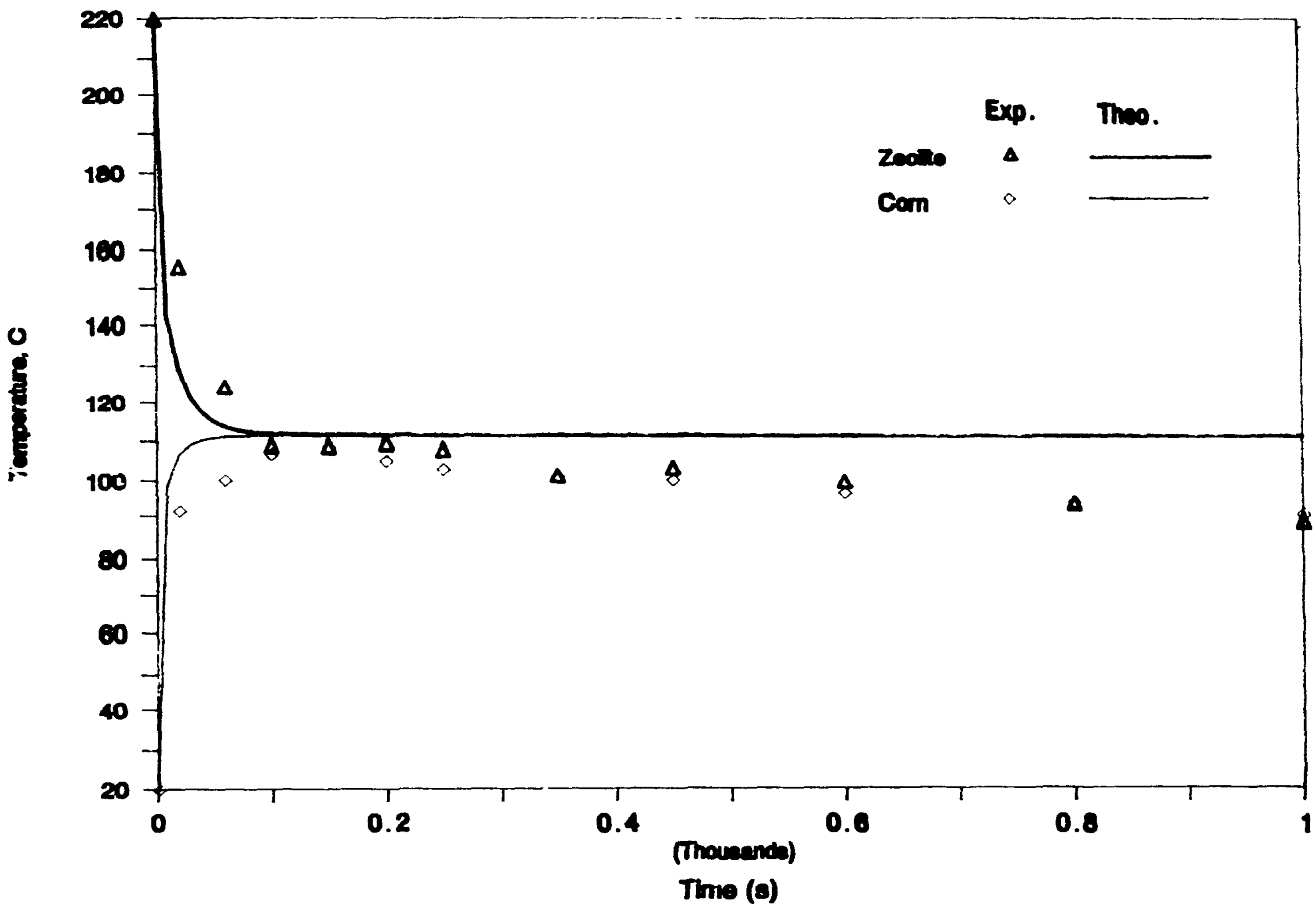


Fig 4.10 Surface temperature of corn and zeolite

(using a thermocouple, which cannot have a perfect contact with the grain surface), (ii) heat loss during the flow of grain from the dryer to the thermos flask, and (iii) the assumption of a perfect adiabatic process, which means that the mixture temperature reaches steady state and remains constant. Although every effort was made to simulate an adiabatic process, there was some heat loss in the dryer. However, despite the fact that the model does not include the effect of mass transfer, the numerical solution of the heat transfer problem provides some insight into the process. The accuracy of the theoretical prediction of the temperature in the mixture may be improved by taking into consideration the coupled effect of mass transfer in the process.

4.6 Summary and conclusions

The numerical solution of heat transfer in the mixture of corn and zeolite with the assumption of perfect thermal contact gives an excessively high grain surface temperature, and it was therefore necessary to use a finite contact resistance. Two parameters of importance in the process are the effective thermal conductivity and the heat transfer coefficient between the particles of the heating medium and the medium being heated. The effective thermal conductivity of the heating medium was determined experimentally. An empirical relation reported for an analogous heat transfer process was used to calculate the heat transfer coefficient. The results of the numerical calculation of the grain surface temperature were generally higher than the experimental values, the difference being attributed to the method of temperature measurement. However, considering the practical limitations of such experiments, the results are considered in reasonable agreement with the theoretical values. The theoretical values may be improve by considering the coupling effect of mass transfer.

CHAPTER FIVE

KINETICS OF MOISTURE SORPTION IN CORN-ZEOLITE MIXTURES

The causes of events are more interesting than the events themselves.

— *Cicero (106 - 43* BC)

5.1 Diffusivity of moisture

Understanding of the drying rate and the diffusivity of moisture in a material is essential to the design of a dryer for that material. The diffusivity depends on moisture concentration and temperature. Experimentally determined diffusivity referred to as effective diffusivity (D_e), is used to estimate the moisture transport property of the material (Saravacos and Raouzeos, 1986). In this chapter, the kinetics of drying grain com during intimate contact with granular zeolite and, in particular, the values of effective diffusivities, are reported.

It is known that grain drying normally takes place only in the falling rate period, unless there is some condensation on the grain surface (e.g. rain) or the grain is harvested immaturely (Brooker et al., 1974). The drying rate is therefore accepted as being controlled by the rate of internal moisture movement, since the initial moisture content is below its critical moisture content. Assuming that moisture migration takes place by diffusion, we have:

$$\frac{\partial U}{\partial t} = \nabla(D_e \ \nabla U) \qquad \text{.....................} \quad (5.1)$$

where

U = local moisture content at time t
D_e= moisture diffusivity within the grain
t = drying time.

Pabis and Henderson (1961) regarded the corn kernel being brick-shaped; some other researchers have assumed a spherical shape for corn kernel. Fortes and Okos (1981) observed that the shape and size of corn kernels depend on their location on the cob: kernels from the centre have a brick-like shape while those from the tip are more spherical. In their study, the latter authors assumed a spherical shape for corn kernels. Considering a corn kernel as a spherical object of radius R, the solution of Eqn 5.1 as given by Newman (1931b) follows:

$$\frac{U - U_{eq}}{U_i - U_{eq}} = \frac{6}{\pi^2} \sum \frac{1}{n^2} \exp\left[- \pi^2 n^2 \left(\frac{D_e t}{R^2}\right)\right] \qquad \text{.....................} \quad (5.2)$$

For long drying times, Eqn 5.2 can be simplified and approximated by the first term:

$$\frac{U - U_{eq}}{U_i - U_{eq}} = \frac{6}{\pi^2} \exp\left(- \pi^2 D_e \ t/R^2 \right) \qquad \text{.....................} \quad (5.3)$$

The variables U, U_i, U_{eq}, R and t can be determi· l experimentally and therefore the value of D_e can be obtained for a particular moisture content. The average value of effective diffusivity can be determined graphically by plotting $(U - U_{eq})/(U_i - U_{eq})$ vs. time on a semi-log scale.

5.2 Materials and methods

5.2.1 Experimental materials

The unique properties of zeolites have resulted in a variety of applications of this material. For example, as mentioned in Section 2.5.2, natural zeolites have been fed as supplemental diets to livestock, poultry and fish. It was therefore decided to use natural zeolites for our experiments as they would not have any deleterious effects on the health of animals to which the processed grain would be fed.

The natural zeolite used was chabazite (Catalogue No. 27121) obtained from Minerals Research, New York. It was mined in Christmas, Arizona; it was sieved and had a particle size in the range 10 - 20 mesh (0.84 - 1.68 mm). Chabazite was selected beca··· this type of zeolite is considered to possess such favorable properties as high thermal stability and a large void volume. It was decided to use a medium-to-grain mass ratio of 3:1 so that the amount of adsorbing medium would be significantly higher than the stoichiometric requirement. Thus, the amount of adsorbing medium would not pose any constraint and be a limiting factor for the removal of moisture.

5.2.2 Procedure

Drying experiments were conducted in a dryer, which was basically a rotating drum designed for batch processing (Fig. 4.7). Naturally moist grain corn (yellow dent) was the material to be dried. The amount of corn dried in each experiment was 500 g. Each sample was taken from a bag containing enough corn for drying (500 g) and some for determining the initial moisture content. Naturally moist yellow corn was shelled, put in sealed plastic bags and kept in a refrigerator at 2°C. A bag of corn was taken out of the refrigerator several hours before each drying experiment so that it would reach ambient temperature of about 20°C.

Five initial medium temperatures (140, 160, 180, 200 and 220°C) were used. The medium was placed in enamelled trays and heated overnight at the required temperature. When the drying experiments with one initial medium temperature had been completed, the oven was adjusted to another temperature level.

The grain corn was poured into the dryer, and the heated medium was added. Filling and emptying the dryer took very little time. The dryer door was closed and the motor was switched on. The residence time for each experiment was taken from the time of closing the door to the time of opening the door.

When the residence time for a particular drying period was over, the corn and the medium were separated. Provisions were made such that the separation process did not take more than a couple of seconds. The temperatures of the zeolite and the processed corn were then measured and samples of the grain were taken for moisture content determination. The ASAE standard for moisture content determination of grains (ASAE, 1983) was followed.

5.3 Results and discussion

5.3.1 Estimation of diffusivity for long residence times

The curves for moisture content of grain vs. time indicate that the amount of moisture removed by the medium was larger at higher medium temperatures for the same residence times. The drying curves for corn for the initial zeolite temperatures of 140, 180 and 220°C are presented in Fig. 5.1. Similar results for the initial zeolite temperatures of 160 and 200°C are given in Appendix E1. While it is reported that the diffusivity of moisture in zeolites has an Arrhenius type temperature dependence (Barrer and Fender, 1961): $D = D_o \exp(-E/\mathcal{R}T)$, it is also known that the total adsorption capacity of the desiccant deceases with increased temperature (Kersh, 1961; Flanigan, 1984). Furthermore, it is known that the diffusivity of moisture in corn increases at higher temperatures (Pabis and Henderson, 1961; Chittenden and Hustrulid, 1966). In a drying situation where heated zeolite is mixed with grain corn, the moisture removal will therefore depend on the overall diffusion of moisture in the grain-medium mixture.

Equation 5.3, and its analogue (Fig. 5.2), were used to determine the values of effective diffusivity. The values of effective diffusivity using this approximation ranged from 1.012×10^{-5} cm²/s, when using 140 °C initial medium temperature (about 80 °C grain temperature), to 3.127×10^{-5} for the initial medium temperature of 220 °C (about 100 °C grain temperature).

As reported in the literature the values of effective diffusivity for corn in conventional drying differ because of different operating conditions and different assumptions in the analysis. Pabis and Henderson (1961) reported values in the range of 2×10^{-5} and 8×10^{-5} cm²/s for the coefficient of internal moisture diffusion in corn

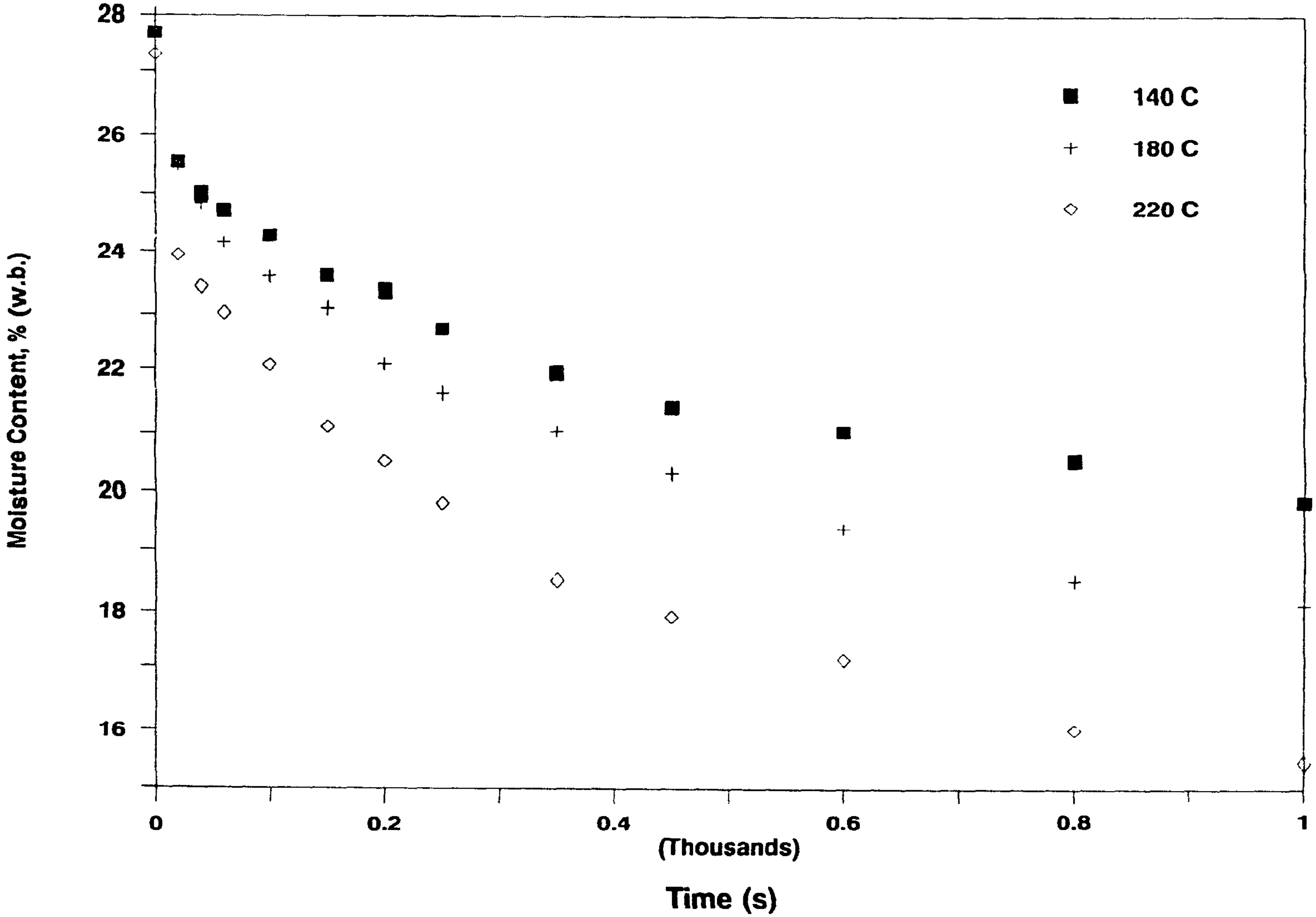


Fig 5.1 Drying curves for corn mixed with heated granular zeolite

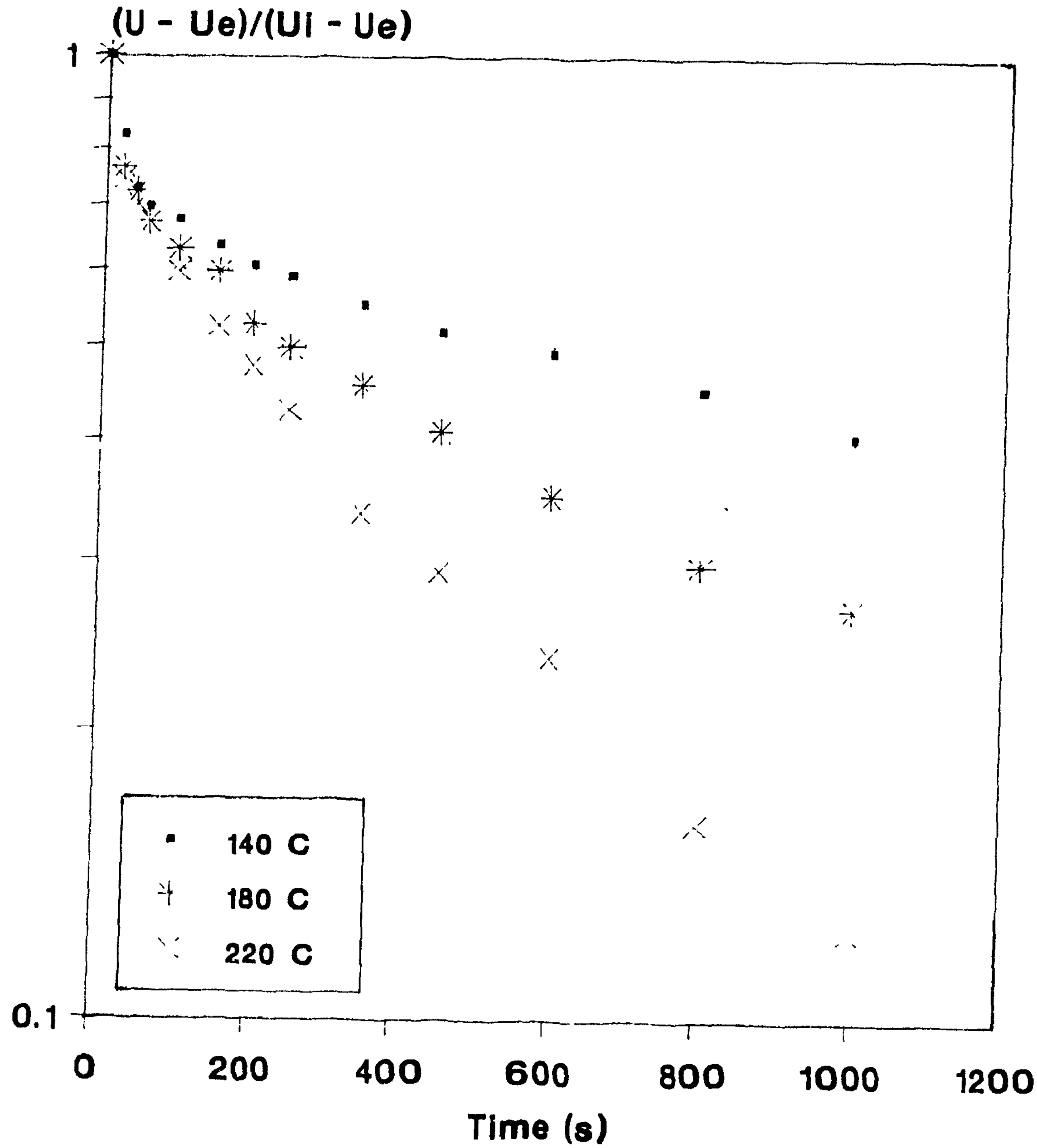


Fig. 5.2 Moisture ratio vs time

at kernel temperatures of up to 71°C (160°F). The values given by Chittenden and Hustrulid (1966) are lower: 0.376 x 10^{-6} to 1.092 x 10^{-6} cm^2/s, and so is their drying air temperature (37.78°C (100°F)). The model developed by Syarief, et al. (1987) for moisture diffusion in a corn kernel is a function of the moisture content and takes the form: $D(M) = A_0 \exp(0.086\ M)$, where the values of A_0 differ for different corn components, such as germ, endosperm, etc. The diffusion coefficient values they have reported for these components are in the order of 8 x 10^{6} to 5 x 10^{-8} cm^2/s.

Thus, the values of effective diffusivity for grain corn we obtained in this study are higher than those reported for air drying (Table 5.1).

Comparison of our results for the diffusivity of moisture in corn with those for zeolite sheds light on the nature of moisture sorption in zeolite-corn mixtures. Barrer and Fender (1961) found the value of effective diffusivity in chabazite at 80°C to be 8.30 x 10^{-5} cm^2/s, much higher than the 3.98 x 10^{-6} cm^2/s value we obtained for corn at the same temperature. Because of the Arrhenius type dependency of diffusivity of moisture in zeolite on temperature, the effective diffusivity will be even higher at higher temperatures. Therefore, it is believed that in this drying process the main resistance to moisture diffusion is offered by the corn kernel, and that the diffusivity of moisture in zeolite is not a limiting factor. Furthermore, as the medium temperature rapidly drops in the heat exchange process with the grain, the adsorption capacity of the zeolite is improved greatly and does not cause a bottleneck.

Table 5.1 Some effective diffusivity values reported for corn

D_e (cm²/s)		Reference
0.1 - 1.45 E -6	R.H. = 28 % T = 27 - 38°C $U_{c,i}$ = 15 - 60 % (d.b.)	Chittenden and Hustrulid (1966)
2.0 - 6.9 E-5	T = 38 - 71°C	Pabis and Henderson (1961)
D(U) = A exp(0.086 U) where, U - Moisture content, % (d.b.) A - a constant depending on the corn component, e.g. germ, endosperm, etc.		Syarief et al. (1987)

5.3.2 Estimation of diffusivity for short residence times

It should be noted that throughout this chapter the solution given to Eqn 5.1 was based on the assumption of large values of t. For small values of t, Ruthven (1984) has given the following solution in terms of fractional approach to equilibrium:

$$\frac{U - U_\infty}{U_i - U_\infty} = 6\left(\frac{D_e\, t}{R^2}\right)^{1/2} \left\{\pi^{1/2} + 2 \sum \mathrm{ierfc}\left(\frac{n R}{\sqrt{D_e\, t}}\right)\right\} - 3\, \frac{D_e\, t}{R^2} \qquad \text{.......... (5.4)}$$

Ruthven (1984) stated that for $\frac{U - U_\infty}{U_i - U_\infty} < 0.3$ Eqn 5.4 can be approximated by:

$$\frac{U - U_\infty}{U_i - U_\infty} \approx \frac{6}{\pi} \left(\frac{D_e\, t}{R^2}\right)^{1/2} \qquad \text{.................... (5.5)}$$

A plot of fractional uptake vs. $\sqrt{t}$ for the first 60 s is shown in Fig. 5.3. The values of effective diffusivity were found to be in the range of 2.6 x 10^{5} to 5.6 x 10^{-5} cm^2/s. The grain temperature in this period rose rapidly from about 20°C to 75 and 100°C, for initial medium temperatures of 140 and 220°C, respectively. Therefore, while the assumption of an isothermal process for long drying times is justifiable, for short drying times a suitable methodology must be derived for dealing with the varying grain temperature and moisture content.

How will the kinetics of moisture sorption be affected in real life with the presence of foreign materials in the harvested grain? If there is any gooey material (Obleck - like[1]), which is not very likely in grain coming directly from the field, it will certainly affect the overall picture but small amounts of dirt that may be present in

1 Bartholomew and Obleck, by Dr Seuss, Random House, N.Y., 1949, 46 pages.

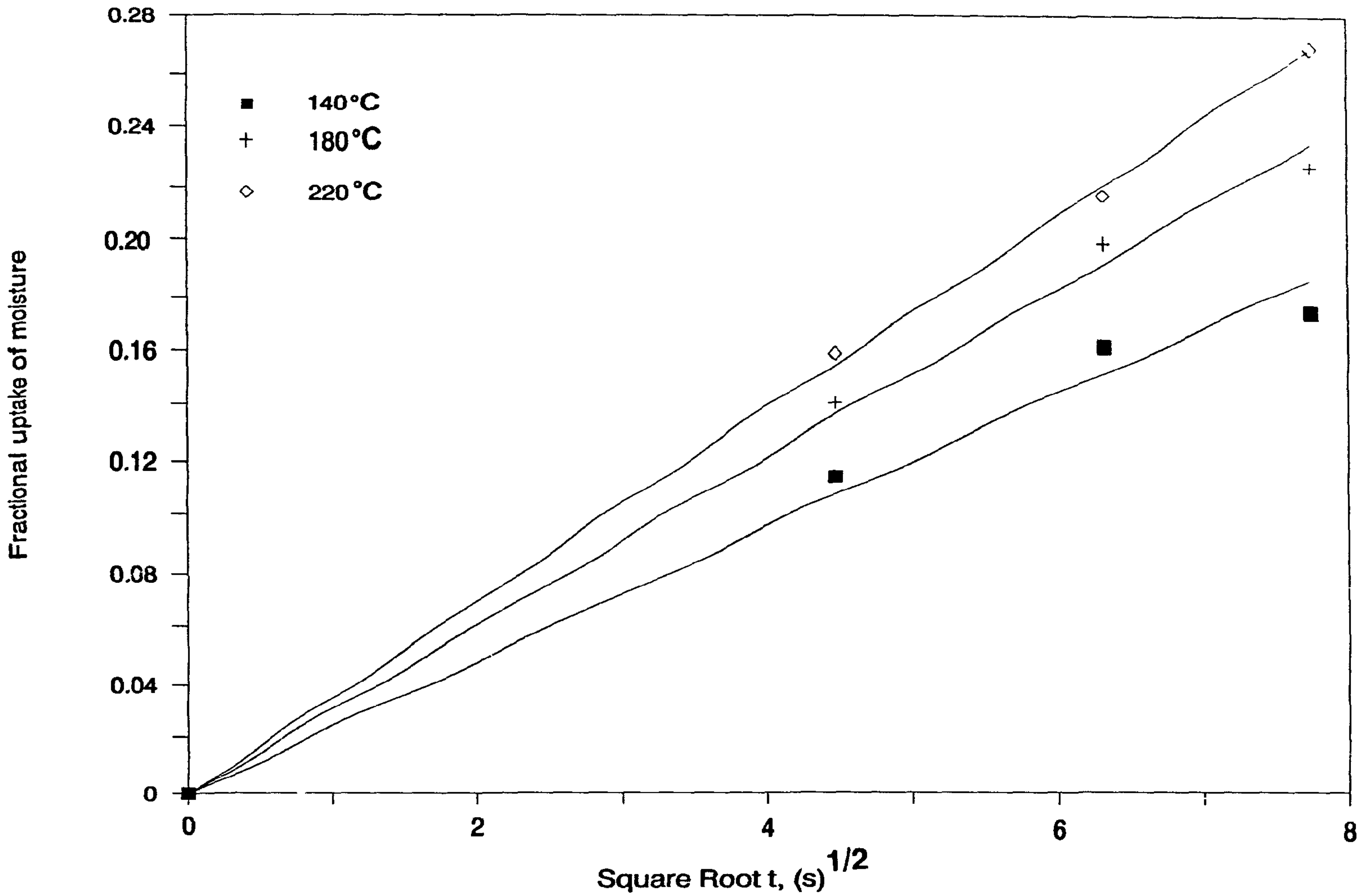


Fig 5.3 Fractional uptake of moisture for short residence times

the grain should not cause a major problem, since dirt due to heat and attrition will not stick to zeolite. Farouk et al. (1981) studied the effect of dust on the moisture adsorption characteristics of silica gel, molecular sieves, and activated alumina and concluded that the presence of 5 percent dust did not affect the moisture sorption capacity of the desiccants but that, compared to a dust-free desiccant, the presence of dust increased the sorption time by 50 percent.

5.4 Summary and conclusions

The kinetics of moisture sorption in corn-zeolite mixtures was investigated using an adiabatic dryer. In this part of the study, a natural zeolite (chabazite) was employed as the heating medium for drying corn. Results of the drying experiments indicated that the diffusivity values for corn were 1.012×10^{-5} - 3.127×10^{-5} cm^2/s with zeolite at temperatures of 140 - 220°C. These values are lower than those for zeolite. Therefore, it is believed that the diffusion of moisture in the corn itself represents the main resistance to the transfer of moisture, thus implying that the effective diffusivity of zeolite, for the range of values involved in these experiments, is not the limiting factor.

CHAPTER SIX

NUMERICAL SOLUTION OF COUPLED HEAT AND MASS TRANSFER EQUATIONS

> It is the mark of an instructed mind to rest satisfied with the degree of precision which the nature of the subject permits and not to seek an exactness where only an approximation of the truth is possible — *Aristotle* (384 - 322 BC)

6.1 Introduction

Mathematical modeling of physical processes is a major subject area for scientific endeavor. The two most important models used in the drying of solids are Fourier's heat conduction and Fick's diffusion equations. These equations are referred to as phenomenological laws which describe energy and mass transfer in the form of proportionalities (Johnson and Hassler, 1968).

In the past, researchers have very often used either of these equations to describe the process of drying. The pioneers in research on the drying of solids (Lewis, 1921; Sherwood, 1929; Newman, 1931a) regarded drying as being mainly a process of moisture diffusion, without taking into consideration the heat transfer aspect of the process.

In more recent times, too, for the analysis of the drying process, some researchers have assumed that the temperature gradient within the small grains is insignificant and therefore the thermal diffusion term was omitted (e.g. Meiring et al., 1971). Özisik (1977) stated that if the value of the parameter hl/λ_s (Biot number) is less than 0.1, then the spatial variation of temperature can be neglected.

For small cereal grains, the assumption that the Biot number is smaller than 0.1 may be acceptable but for artificial drying of corn this assumption results in significant error. Given that the heat transfer coefficient in air drying of corn, $h \approx 50\ W/m^2\ K$, and $l \approx 4 \times 10^{-3}$ m (Fortes and Okos, 1981), and $\lambda_s \approx 0.17$ W/m K (ASAE, 1983), the Biot number will be larger than unity. With a larger heat transfer coefficient, the value of the Biot number can be even higher in solid-medium drying.

The term effective diffusivity describes the overall diffusivity of moisture in the mixture; the diffusivities of moisture in the corn kernel and in the granular zeolite were not considered separately. The basic assumption used to simplify the mathematical problem was to consider the moisture transfer as an isothermal diffusion process. This assumption was acceptable for longer mixing times (based on the temperature history of the mixture) but for shorter times the temperatures of the grain corn and zeolite both changed rapidly. Therefore, as mentioned in Chapter Five, some other models should be employed so that the variation of the temperature could also be treated adequately.

It is well known that drying is a process of simultaneous heat and mass transfer. Luikov (1966) stated that "Mass transfer in wet bodies cannot be separated from heat transfer and the phenomena of heat and mass transfer must be considered in their inseparable association." In this chapter, a mathematical model which involves both heat and mass transfer is discussed. This system of differential equations furthermore contains terms describing the interaction of the two processes.

6.2 Theories of drying

There are several theories regarding the mechanism of moisture transfer during drying of solids. Following is a brief discussion of four main theories: (i) liquid diffusion, (ii) capillary flow, (iii) combined capillary flow and vapour diffusion, and (iv) thermal diffusion.

Liquid diffusion is by far the most widely used theory for moisture transfer in solids. It involves the assumption that the gradient of moisture concentration is the driving force. This is basically the application of Fick's law. In the area of grain drying, many researchers have used this theory.

Hougen et al. (1940) discussed the limitations of the diffusion equation in drying of solids. They stated that water above the saturation point of fibres, such as textiles and paper, moved by capillarity.

Harmathy (1969) developed a theory for simultaneous heat and mass transfer. He stated that both capillary flow and vapour diffusion are the mechanisms of moisture transfer at the beginning of the falling rate period.

Philip and De Vries (1957) studied the movement of moisture in a porous medium under temperature gradient. Based on classical thermodynamics they derived relations for vapour diffusivity and liquid diffusivity. Luikov (1966), utilizing the thermodynamics of irreversible processes approach, developed a theory of coupled heat and mass transfer during drying of solids.

Among the theories of drying, of particular interest to us is the model developed by A.V. Luikov and its application to agricultural materials. That model was successfully used by Hussain et al. (1973) in their study on drying rice; they reported that the numerical solution of the system of equations was in good agreement with their experimental observations. Rossen and Hayakawa (1977) used the Luikov system of equations to determine the distribution of temperature and moisture in wheat during storage. They pointed out that by using the thermodynamics of irreversible processes approach, Luikov's model "has the intrinsic advantage of obviating the need to assume one or more overriding mechanisms of internal moisture diffusion."

6.3 Coupled heat and mass transfer

6.3.1 Basic concepts

A transfer process, such as heat conduction or mass diffusion, can be expressed by a linear law given as:

$$\mathbf{J} = L\,\mathbf{X} \qquad (6.1)$$

where **J** is the flow or flux (e.g., rate of heat transfer), **X** the gradient of potential (in our example, gradient of temperature) and L a scalar quantity dependent on the properties of the material (in this case, thermal diffusivity).

Hearon (1950) stated that when two or more of these phenomenological processes take place at the same time, their interaction results in new effects not described by the original phenomenological laws. This can be written as:

$$J_1 = L_{11} X_1 + L_{12} X_2$$
$$J_2 = L_{21} X_1 + L_{22} X_2 \qquad (6.2)$$

6.3.2 Luikov's Model

Luikov and Mikhailov (1961) describe a system of differential equations of heat and mass transfer (also known as Luikov's system of differential equations). Based on thermodynamics of irreversible processes and Onsager's reciprocal relations (Onsager, 1931), they developed the following model:

$$\frac{\partial U}{\partial t} = \alpha_M \nabla^2 U + \alpha \, \delta \, \nabla^2 T \qquad \ldots\ldots\ldots\ldots \quad (6.3\text{-a})$$

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T + \frac{\varepsilon_1 H}{c_p} \frac{\partial U}{\partial t} \qquad \ldots\ldots\ldots\ldots \quad (6.3\text{-b})$$

where α - thermal diffusivity
α_M - moisture diffusivity
δ - thermogradient coefficient
ε_1 - phase change criterion
H - heat of adsorption/desorption

Luikov and Mikhailov (1961) considered α_M to be constant and provided a solution for the system of differential equations with constant boundary conditions. The diffusivity of moisture in corn kernels and zeolite particles will depend on their moisture content and the rates of heat and mass transfer are coupled at the boundary.

In the following section, the parameters of heat and mass transfer for the system under study, which involves the drying of moist corn by mixing with heated granular zeolite, will be discussed.

6.4 Description of the parameters

In this section we present the numerical values, or relations, for the parameters of the system of differential equations with specific reference to the drying of corn in a mixture of heated zeolite.

6.4.1 Moisture diffusivity (α_M)

Following Luikov's nomenclature, mass diffusivity in the original equation was referred to by α_M. Since we use subscripts to denote zeolite and corn, it will be clearer to adhere to the more customary notation of D for diffusivity of moisture.

The effect of temperature and moisture on diffusivity of moisture in a corn kernel was discussed in Chapter Five. The values of effective diffusivity, using an experimentally determined moisture ratio, employed a relation based on the assumption of a semi-infinite medium for the drying medium. This assumption will yield values of effective diffusivity higher than the actual values. However, in Chapter Five, the diffusivity of moisture in corn was found for the sake of comparison with that of zeolite. The conclusion that the diffusivity of moisture in corn is lower than that of zeolite will not be contradicted by using any other approach which may yield even smaller values of moisture diffusivity in corn.

For more accurate values of moisture diffusivity in corn kernels immersed in zeolite, account must be taken of the finite mass of zeolite. On the diffusion of moisture from a sphere to the surrounding medium of limited volume, i.e. the concentration of the adsorbing medium changing as the process of adsorption proceeds, Crank (1975) presented the following relation:

$$\frac{U - U_\infty}{U_i - U_\infty} = 1 - \sum \frac{6\,\Lambda(\Lambda + 1)\exp(-Dq_n^2\, t/R_1^2)}{9 + 9\,\Lambda + q_n^2\,\Lambda^2} \qquad \text{.................... (6.4)}$$

where q_n is a non-zero root of the transcendental equation, $\tan q_n = \dfrac{3q_n}{3 + \Lambda q_n^2}$

and $\Lambda = \dfrac{3\,V}{4\pi R_1^2}$, where V is the volume of the surrounding medium.

The values of U, U_∞, U_i, t, V and R_1 are known quantities which can be determined experimentally. Hence, the values of effective diffusivity can be determined from Eqn 6.4. These experimentally determined values of diffusivity, which take into account the effect of limited mass of zeolite, were incorporated in the computer program. The values of effective diffusivity of moisture in corn were in the range of 2.5×10^{6} to 9.0×10^{-6} cm^2/s for T_{zi} = 140°C, and 1.05×10^{-5} to 6×10^{-6} cm^2/s for T_{zi} = 220°C.

As mentioned earlier, according to Barrer and Fender (1961), the diffusivity of moisture in zeolite has an Arrhenius type temperature dependence, i.e. $D = D_0 \exp(-E/\mathcal{R}T)$. They also reported that for chabazite $D_0 = 1.2 \times 10^{3}$ cm^2/s and the time constant $E/\mathcal{R} = 1.7567 \times 10^{3}$ s^{-1}. The expression for the Arrhenius type behavior of moisture diffusion in zeolite was also incorporated into the computer program for the numerical calculation of coupled heat and mass transfer. Typical temperature and moisture profiles in the mixture as a function of time and the space coordinate are given in Section 6.6.

Like the temperature profile in the grain, the moisture content cannot be measured accurately with our existing instrumentation. Therefore, the average moisture of the corn kernels (Section 6.6) was determined by gravimetric analysis. The grain average moisture content predicted by the model is in good agreement with the observed values. It should be pointed out that a constant diffusivity value, particularly if the value is taken after long drying times (low moisture content), would bring about large errors, especially in the early stage of drying.

6.4.2 Phase change criterion (ε_1)

The phase change criterion indicates the phase(s) (liquid or vapor) in which moisture moves in the solid material, and whether there is a phase transformation which will cause a change in the temperature of the material. The value of ε_1 ranges from zero to one; zero for no phase change and unity denoting a complete transformation from one phase to another. Here, the moisture evaporated from the corn will be adsorbed by zeolite; this adsorbed moisture is the vapor condensed on the solid surface. Thus a complete phase transformation ($\varepsilon_1 = 1$) occurs.

For the case of desorption, i.e. drying of corn, however, the situation is more complicated. In section 6.2 some of the theories for the movement of moisture in solids was discussed. Some investigators have suggested that moisture moves in solids by liquid diffusion (e.g. Becker and Sallans, 1955; Pabis and Henderson, 1961; Young and Whitaker, 1971). Others supported the theory of moisture movement in the vapor phase (e.g. Gurr et al., 1952; Kuzmark and Sereda, 1957). Luikov (1966) remarked that

ε_l can be determined experimentally. Theoretically, $\varepsilon_l = J_V/(J_V + J_L)$, where J_V is vapor flux and J_L is liquid flux. Fortes and Okos (1981) derived relationships for J_L and J_V based on the thermodynamics of irreversible processes. They reported that for low temperature (26.7°C) drying of corn, liquid flux was higher than vapor flux. For their intermediate temperature (75°C), liquid flux and vapour flux were of the same order of magnitude. Finally, for temperatures in the range of 125 - 150°C, liquid flux was always lower than vapor flux.

In our experiments, we observed that the corn surface temperature was in the range of 70 - 100°C. Therefore, following the work of Fortes and Okos (1981), we will use $\varepsilon_l = 0.5$ for the numerical value of the phase change criterion for drying corn.

6.4.3 Thermogradient coefficient (δ)

Luikov and Mikhailov (1961) defined the Soret coefficient as δ/c_T, where c_T is called specific mass capacity. They stated that in unsteady state heat and mass transfer, the Soret coefficient can be extremely small. In terms of the order of magnitude of the thermogradient coefficient, Hussain et al. (1970) reported that for corn with a moisture content of 12 - 20 percent (w.b.) at 60°C, δ was 48 - 96 x 10^{-6} 1/K. Considering that δ is multiplied by D_c, yet another small number, the second term on the right side of Eqn. 3-b can be ignored.

6.4.4 Heats of adsorption/desorption

The heat of vaporization of free water at different temperatures and pressures is readily available in the literature. Due to the nature of water bound in a grain, the heat of vaporization will be higher than that of the free water. Johnson and Dale (1954) studied the heat of vaporization of moisture in corn. They concluded that for drying corn above 14 percent (d.b.) the heat of vaporization was 1.00 to 1.06 times that of free water. Below 14 percent (d.b.) the heat of vaporization increased, for instance at 10 percent (d.b.) it was 1.15 to 1.20 times that for free water. Since in our drying, experiments, the moisture content was generally higher than 14 percent (d.b.), 1.06 times heat of vaporization of free water was used.

In the process of drying of corn mixed with a desiccant, the moisture sorption involves heat of adsorption and of desorption. The moisture removed from corn will be adsorbed by zeolite, hence the zeolite particles will experience heat of adsorption (wetting). The principle for calculating the heat of adsorption/desorption is based on the Clausius - Calpeyron equation and experimental determination of sorption isotherms. Barrer and Fender (1961) presented their data for isosteric heat of sorption of water on chabazite. For the range of 0.88 - 0.95 degree of saturation, the heat of sorption was 61.128 kJ/mol (14.6 kcal/mol). This is the value which will be used in the subsequent equations.

6.5 Application of the model to grain-zeolite mixtures

The nomenclature for the physical model of the particles of zeolite and grain corn is shown in Fig 6.1. The development of the mathematical model and of the boundary conditions are discussed below.

By neglecting the second term of Eqn. 6.3 - a, the equation reduces to: $\partial U/\partial t = \alpha_M \nabla^2 U$. Substituting the numerical value of ε_1, we will have the following

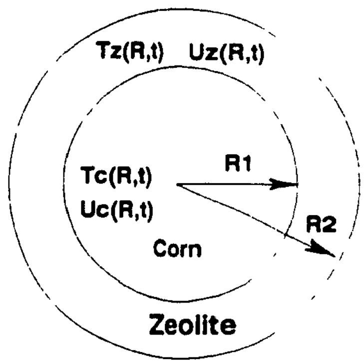


Fig. 6.1 Nomenclature for the heat and mass transfer model

set of equations for corn:

$t > 0 \qquad 0 \leq R \leq R_1$

$$\frac{\partial U_c}{\partial t} = D_c \left(\frac{2}{R} \frac{\partial U_c}{\partial R} + \frac{\partial^2 U_c}{\partial R^2} \right) \qquad \text{(6.5-a)}$$

$$\frac{\partial T_c}{\partial t} = \alpha_c \left(\frac{2}{R} \frac{\partial T_c}{\partial R} + \frac{\partial^2 T_c}{\partial R^2} \right) + \frac{0.5\, H_c}{C_{pc}} \frac{\partial U_c}{\partial t} \qquad \text{(6.5-b)}$$

For zeolite, substituting $\varepsilon_1 = 1$, we will have:

$t > 0 \qquad R_1 \leq R \leq R_2$

$$\frac{\partial U_z}{\partial t} = D_z \left(\frac{2}{R} \frac{\partial U_z}{\partial R} + \frac{\partial^2 U_z}{\partial R^2} \right) \qquad \text{(6.6-a)}$$

$$\frac{\partial T_z}{\partial t} = \alpha_z \left(\frac{2}{R} \frac{\partial T_z}{\partial R} + \frac{\partial^2 T_z}{\partial R^2} \right) + \frac{0.5\, H_z}{C_{pz}} \frac{\partial U_z}{\partial t} \qquad \text{(6.6-b)}$$

Based on the conservation of energy and assuming an adiabatic process we will have the following initial and boundary conditions.

$$R = 0 \qquad \frac{\partial U_c}{\partial R} = 0 \qquad \frac{\partial T_c}{\partial R} = 0$$

$$R = R_2 \qquad \frac{\partial U_z}{\partial R} = 0 \qquad \frac{\partial T_z}{\partial R} = 0 \qquad \text{.....................} \quad (6.7)$$

$$R = R_1 \qquad U_c = U_z \qquad -\lambda_c \frac{\partial T_c}{\partial R} = h\ (\ T_c - T_z\ )$$

Equations 6.5 and 6.6 together with the boundary conditions 6.7 form a system of partial differential equations which are coupled at the boundary. If the diffusivities are considered variable then that will make the system non-linear. No analytical solutions for these equations are known at the present time. Using NMOL as described in section 4.4, the numerical solution of these equations is obtained.

6.6 Results and discussion

The numerical solution of the differential equations of simultaneous heat and mass transfer coupled at the boundary is presented graphically Figs. 6.2 and 6.3. These figures, which correspond to an initial zeolite temperature of 180°C and initial corn temperature of 20°C, are typical of the variation in temperature and moisture content of the mixture as a function of time and the spatial coordinate.

Since it was not practical to measure the temperature in the profile, either for zeolite during mixing or for the corn kernel, comparison between the experimental values and the predicted values are made only for surface temperatures.

The grain surface temperature history (plot of temperature vs. time) for the initial zeolite temperature of 220°C is given in Fig. 6.4. It can be seen that the theoretical values of the temperature are slightly higher than the observed values. The

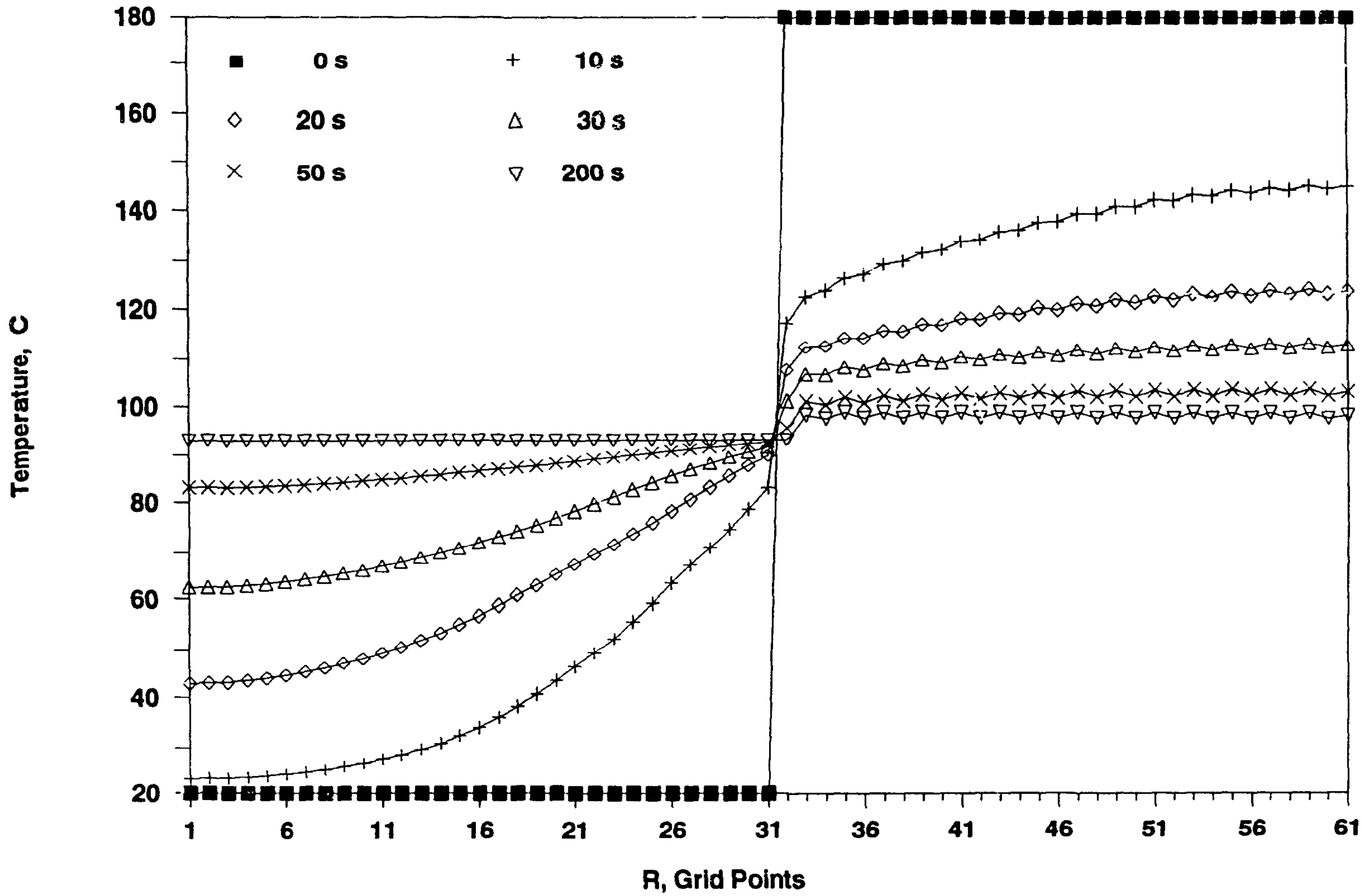


Fig 6.2 Temperature profile in a grain-zeolite mixture

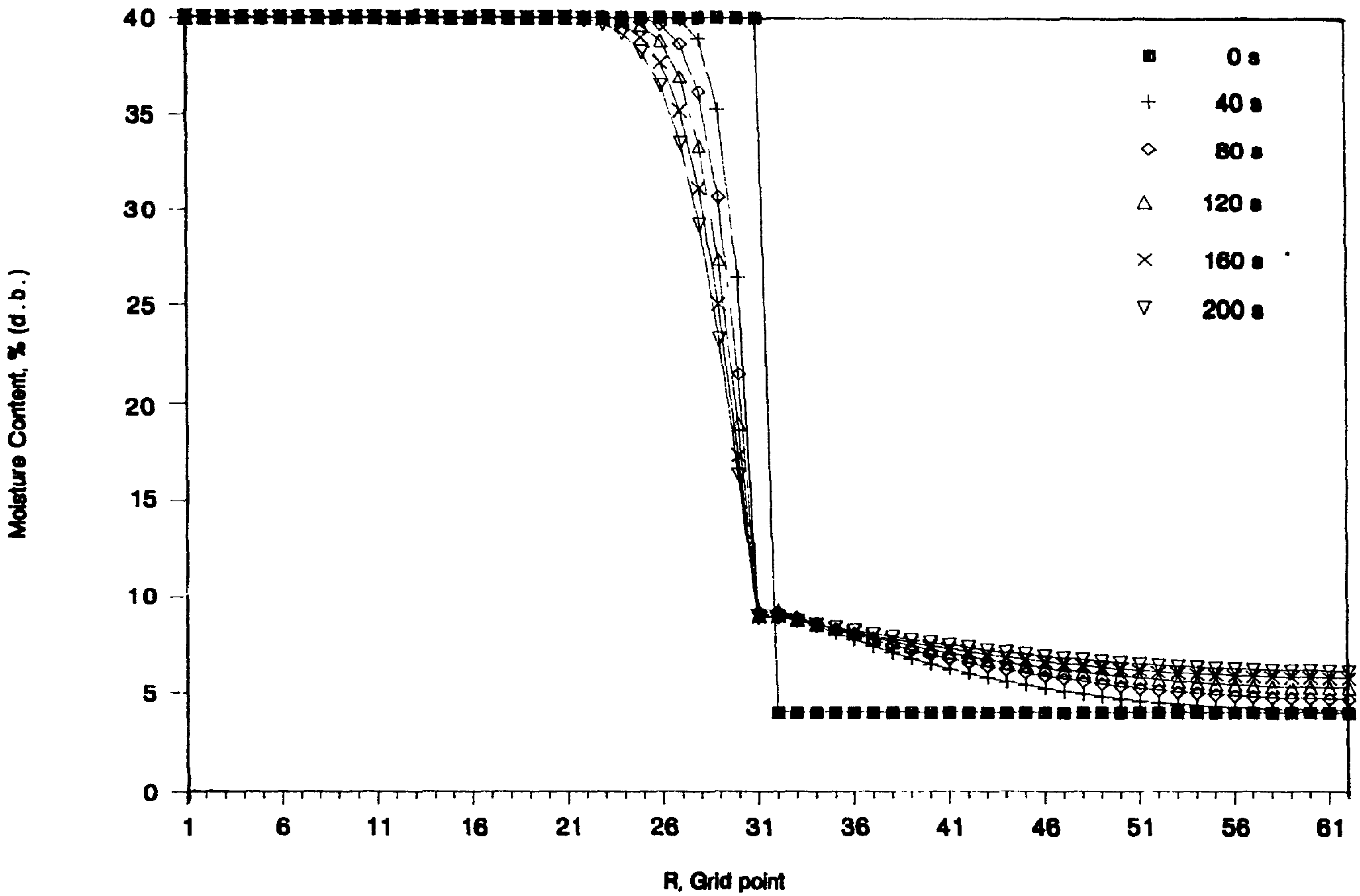


Fig 6.3 Moisture concentration profile in a corn-zeolite mixture (Tzi=180 C)

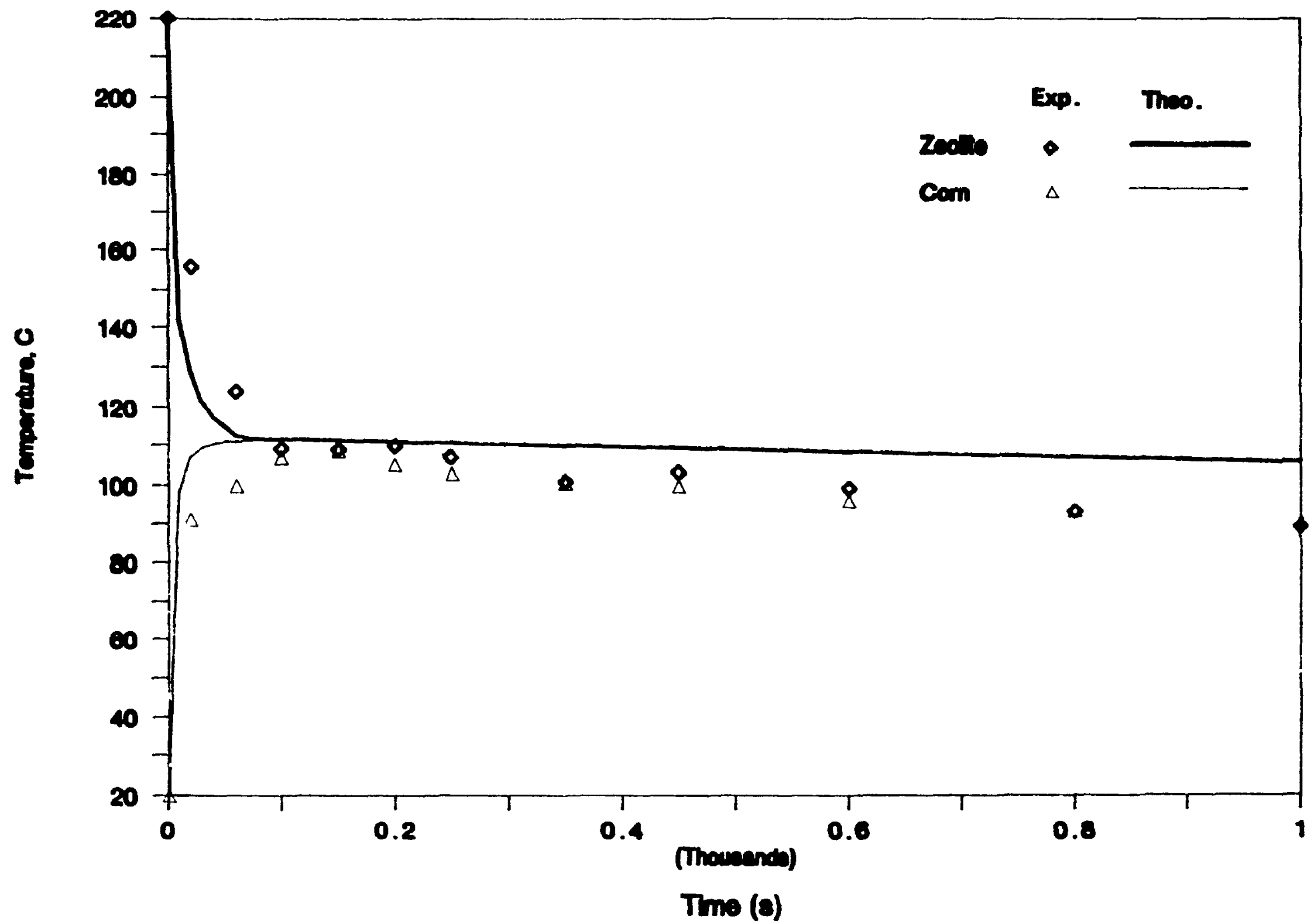


Fig 6.4 Observed and predicted values of corn and zeolite surface temperatures

argument for this type of discrepancy between measured and predicted values of temperature given in Section 4.5 may be reiterated here: experimental limitations. However, it can be seen that by taking into consideration the coupled effect of mass transfer, as shown in this section, the calculated values for corn temperature are lower than the values given in Section 4.5. This may be regarded as an improvement in the accuracy of the model for predicting the grain temperature. However, the effect of coupling did not appear to have significant effect.

Experimentally determined values of diffusivity were incorporated into the computer program. The values of the effective diffusivity of moisture in corn ranged from 2.5×10^{-6} to 1.5×10^{-5} cm^2/s. The expression for the Arrhenius type behavior of moisture diffusion in zeolite was also incorporated into the computer program. Like the temperature profile of the mixture, the moisture content cannot be measured accurately for each incremental volume the way it can be calculated by the model. Therefore, the average moisture content of corn kernels determined by gravimetric analysis was compared with the theoretical values. The observed and theoretical values corresponding to initial medium temperatures of 140, 180, and 220°C are given in Figs. 6.5 - 6.7.

Good agreement can be seen between the observed and predicted values of grain moisture content. However, it should be pointed out that the accuracy of this model, as with any model, greatly depends on the accuracy of the parameters involved. In employing this model, experimentally determined values of several parameters were utilized which may have contributed to the accuracy of final results. In this study the value of ε_1 was taken from Fortes and Okos (1981) and δ was omitted. The values of ε_1 and δ for other materials are not readily available in the literature. This may have

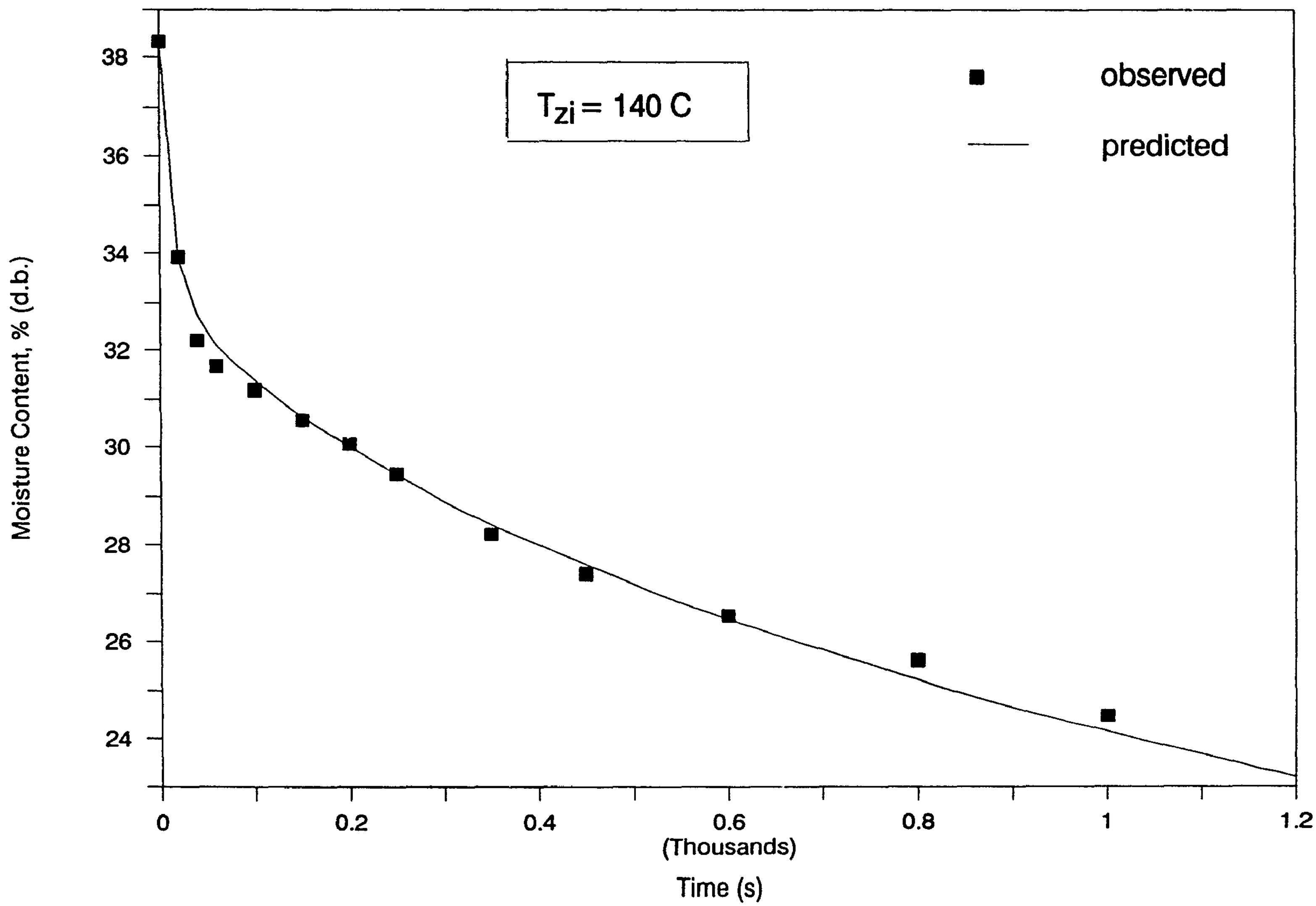


Fig 6.5 Observed and predicted values of corn moisture content

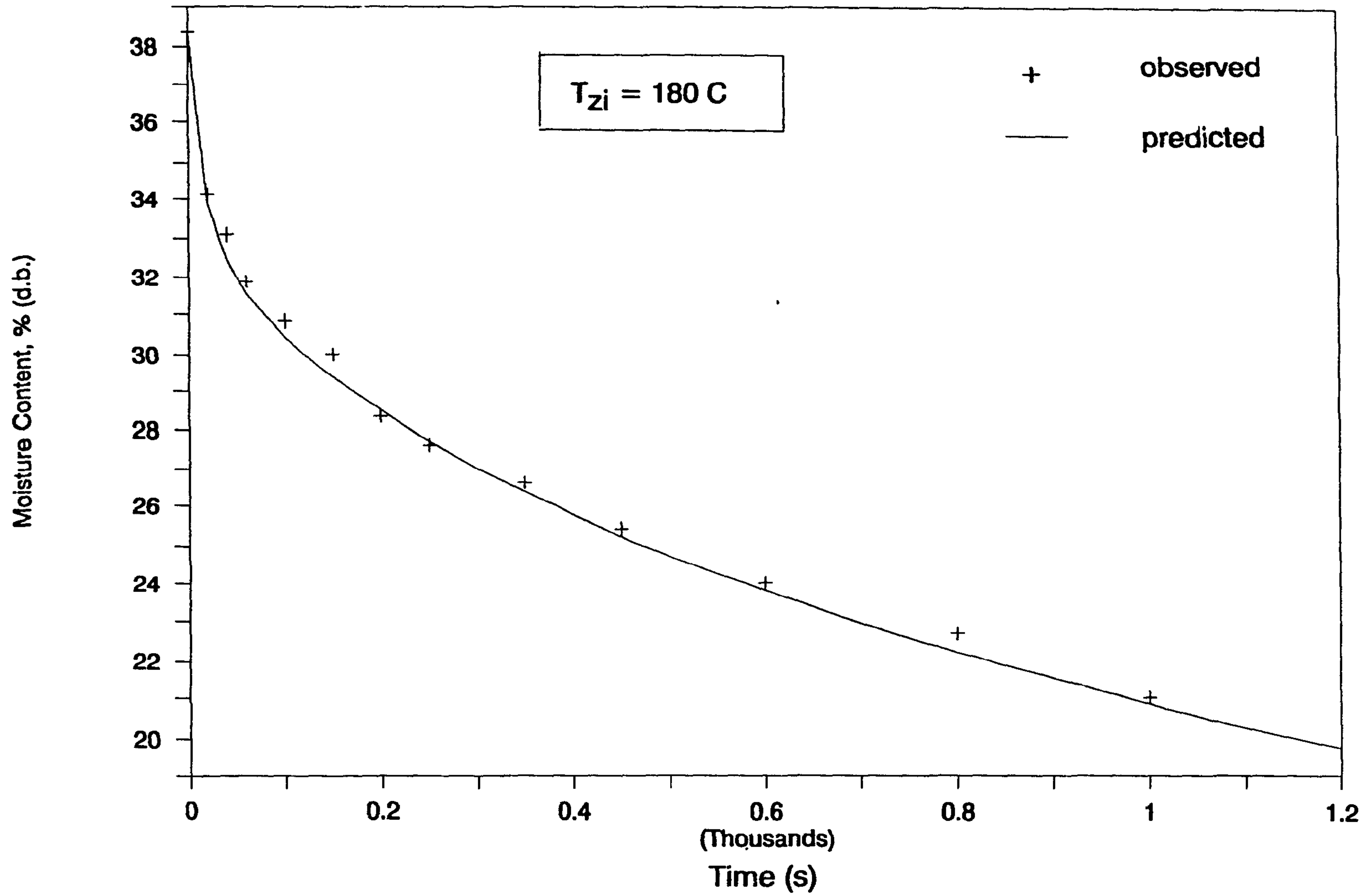


Fig 6.6 Observed and predicted values of corn moisture content

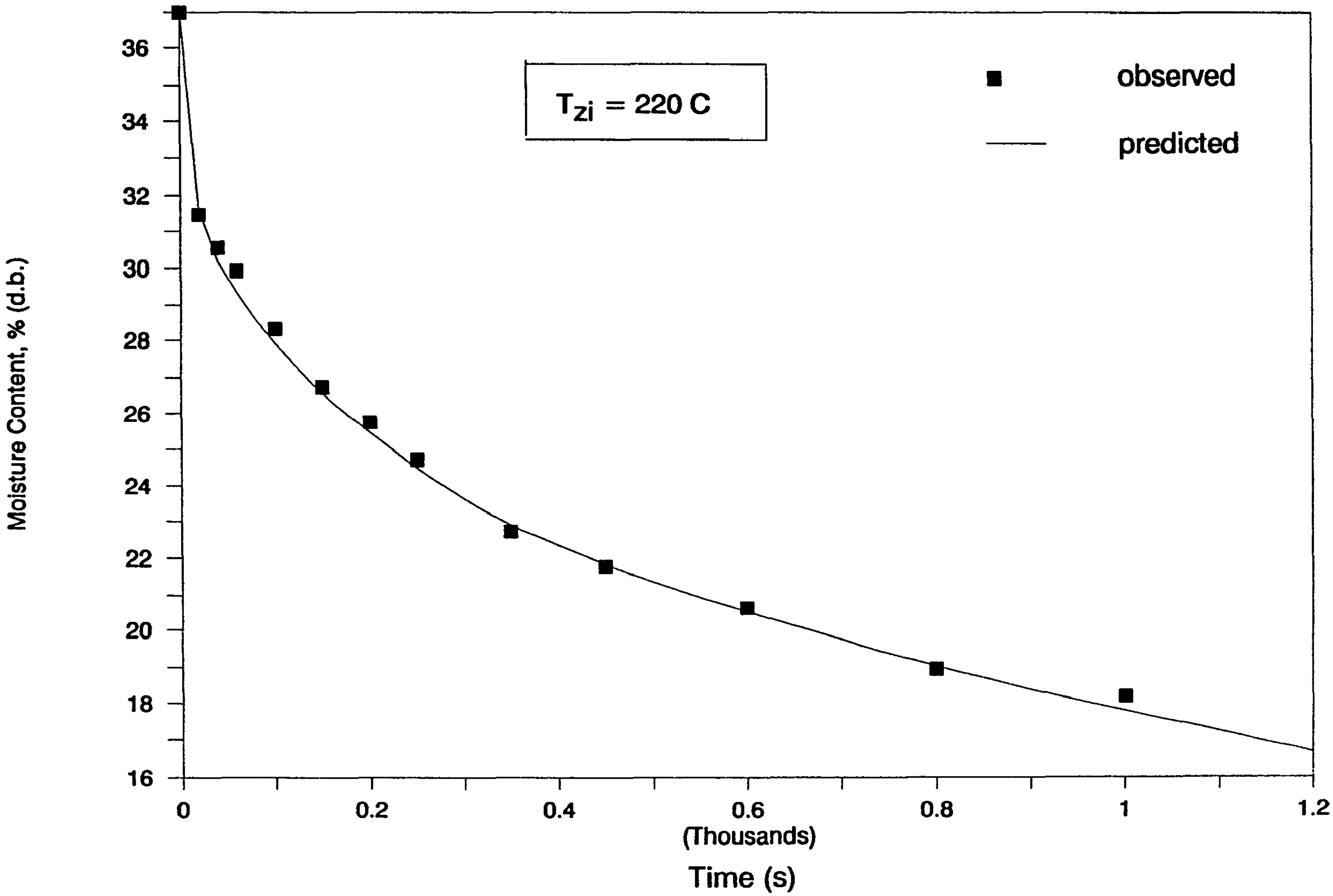


Fig 6.7 Observed and predicted values of corn moisture content

been the major obstacle in applying Luikov's model. In order that Luikov's model can be applied for other crops and other drying situations more work is needed to evaluate these parameters.

6.7 Summary and Conclusions

The application of a system of differential equations developed by A.V. Luikov to simultaneous heat and mass transfer in a zeolite-corn mixture was discussed. The values of the phase change criterion (ε_1) for corn kernels and zeolite were taken to be 0.5 and 1.0, respectively. The thermogradient coefficient (δ) was considered negligible. Experimentally determined values of diffusivity were incorporated into the computer program. The values of effective diffusivity of moisture in corn was in the range of 2.5×10^{-6} to 1.5×10^{-5} cm^2/s. The variable diffusion coefficients of corn and zeolite were substituted in the original equations. These partial differential equations of heat and mass transfer, coupled at the boundary, were solved numerically by NMOL.

Numerical solution of the system of differential equations indicates good agreement between the mixture temperature and moisture content values compared with the observed values. Including the coupling effect of heat and mass transfer, the predicted values of temperature were lower than without it. However, the theoretical values of the temperature were relatively higher than the measured values, the difference being attributed to the measuring method and experimental drawbacks. The theoretical average values of moisture content based on the Luikov's model were in good agreement with experimentally determined values.

CHAPTER SEVEN

EFFECT OF PARTICULATE MEDIUM DRYING ON CORN QUALITY

It is not what the man of science believes that distinguishes him,
but *how* and *why* he believes it. — *Bertrand Russell* (1872 - 1970)

7.1 Introduction

It is well-known that thermal processing will result in some changes in the properties of the processed corn. Depending on the extent of the change, some of these changes are easily detected by inspection while others may require sophisticated laboratory analysis.

As mentioned in the review of the literature on the quality of heat treated corn in Section 2.6, the end use of the corn will determine whether the changes brought about by thermal processing are beneficial or not. It is therefore imperative to recognize the major use of corn.

Corn is essentially considered to be a feed grain (Watson, 1982). In the United States, where about half the world corn is grown, some 90 percent of the unexported corn is used for animal feed (Hodge, 1982). It is believed that in many countries around the world the main use of corn is for animal feed (Watson, 1982). Therefore, new methods of drying corn should be examined in view of the possibility of using the processed corn as material for animal feed.

The following two sections present, results of an *in vivo* analysis, i.e. studies involving live animals (Section 7.2), and a chemical analysis, laboratory studies on the availability of protein in corn (Section 7.3). In section 7.4, the physical attributes of the processed corn will be discussed.

7.2 In vivo *analysis*

The corn for *in vivo* analysis was obtained from the initial experiments conducted to determine the potential of molecular sieves for drying corn (Chapter 3). Details of the drying procedure and the description of the dryer were presented in Section 3.2. For logistical reasons, the corn processed in drying experiments involving a medium-to-grain mass ratio of 6:1 and two drying media, sand and molecular sieve 13X, were used. The operating conditions of these drying experiments are summarized in Table 7.1.

Sufficient corn from each drying process was produced for the feeding experiment. The dried corn was kept in a freezer until all the diets were processed. After grinding in a Wiley Mill using a 1 mm screen and adding other ingredients (Table 7.2), the processed corn was made into pellets. These pellets were fed to young male rats of the Sprauge-Dawley breed and used for *in vivo* digestibility analysis. The diets contained 65.35 percent of dry matter as corn. All ingredients were corrected for dry matter content. DL methionine was added to diets to correct the insufficiency of this amino acid in corn-based diets.

Table 7.1. Drying conditions of processed corn *in vivo* analysis*

Diet	Medium	Drying Time (min)	Medium Temp (°C)	MRP**
1	13X	4	150	6.39
2	13X	3	200	7.96
3	13X	2	250	13.25
4	sand	4	150	4.09
5	sand	3	200	6.37
6	sand	2	250	7.65

* Medium-to-grain mass ratio (6:1)

** Moisture removed, in percentage points

Table 7.2. Composition of the diets fed to rats

Ingredient	% of the total diet
Dried corn	65.36
Casein	11.14
Corn oil	10.00
Alphacel	7.00
Mineral premix	4.00
Vitamin premix	2.20
Choline chloride	0.20
D1-methionine	0.10

Thirty rats (five per diet) were housed in individual cages equipped to collect all faeces and urine. The pellets were fed after six days of adapting the rats to cages. During the first six days (adaptation to cages) the rats were fed a commercial rat chow (Purina). From days 7 to 11, the rats were fed the experimental diets and all intakes, faeces and urine were measured from days 11 to 16. Their body weight and the amounts of feed taken in and faeces excreted were recorded daily. This information was used to find the digestibility of dry matter and crude protein. Results of the *in vivo* digestibility in terms of digestibility of dry matter and digestibility of crude protein are presented in Tables 7.3 - 7.4. When the results were statistically analysed, the nutritive quality of the various processed corn grains did not differ significantly. The comparison was made between the treatments subjected to different initial medium temperatures (150, 200, 250°C), and residence times (2, 3, 4 min) for two types of media (synthetic zeolite and sand). The palatability of the processed corn was not affected by different treatments either (Table 7.3).

Table 7.3. Digestibility of dry matter by rats fed a diet based on treated corn

Diet	Avg. intake (g)	Avg. digestibility (%)	Avg. digestible intake (g)
1*	155.99	81.70	127.47
2	149.44	82.51	123.33
3	157.51	83.29	131.14
4	152.85	82.68	126.35
5	169.07	82.55	139.41
6	162.60	81.96	133.18

* For a description of the drying conditions of these diets refer to Table 7.1.

Table 7.4. Digestibility of crude protein by rats fed a diet based on the treated corn

Diet	Avg. intake (g)	Avg. digestibility (%)	Avg. digestible intake (g)
1*	24.57	86.57	21.27
2	23.02	87.57	20.18
3	24.57	87.16	21.43
4	23.61	87.74	20.72
5	26.21	88.08	23.09
6	25.45	88.09	22.41

* For a description of the drying conditions of these diets refer to Table 7.1.

7.3 *Chemical analysis*

The corn used in this part of the analysis was processed by mixing it with a natural granular zeolite (chabazite). The processes of heating the media and separating them were basically the same as for the synthetic zeolite but different initial media temperatures (140, 160, 180, 200 and 220°C) and residence times (1000 s) were used. Details of the drying procedure and the dryer are given in Section 5.3. The operating conditions are summarized in Table 7.5.

The protein content of the processed corn was assessed by measuring of Kjeldahl nitrogen (AOAC, 1980). The method suggested by Goering and Van Soest (1970) was used to determine the percentage of Acid Detergent Fibre nitrogen in the heat treated and untreated corn. The acid detergent fibre nitrogen indicates the percentage of protein available for digestion (heat-damaged).

Samples of heat-treated and untreated corn were analysed for their protein content. Grain temperatures during the drying process ranged, on average, between 60 and 100°C. Results of acid detergent fibre nitrogen in the protein of processed and untreated corn are presented in Figs. 7.1 and 7.2. It can be seen that with thermal processing there is a clear trend of decreased availability of crude protein in the processed corn. Even though this trend is towards more heat-damaged protein with processing of corn, the total amount of heat-damage was minimal in all samples owing to the low amount of fibre initially present in corn, namely 3.3 to 4.0 percent (Table 7.6).

The quality and nutrient availability of the processed corn are important, but, since the thermal processing had little influence on these characteristics, other factors such as palatability and storability take on greater importance. Kuprianoff (1959) stated that in some instances at low temperature drying (e.g. of paprika) results in a more

Table 7.5. Drying conditions for the corn processed for chemical analysis*

Diet	Medium	Medium Temp. (°C)	Moisture Removed (%)
1	chabazite	140	6.66
2	chabazite	160	8.14
3	chabazite	180	9.70
4	chabazite	200	12.27
5	chabazite	220	14.61
6	sand	140	4.10
7	sand	160	4.38
8	sand	180	4.87
9	sand	200	5.12
10	sand	220	6.72

* Drying time = 1000 s, medium-to-grain-mass ratio = 3:1

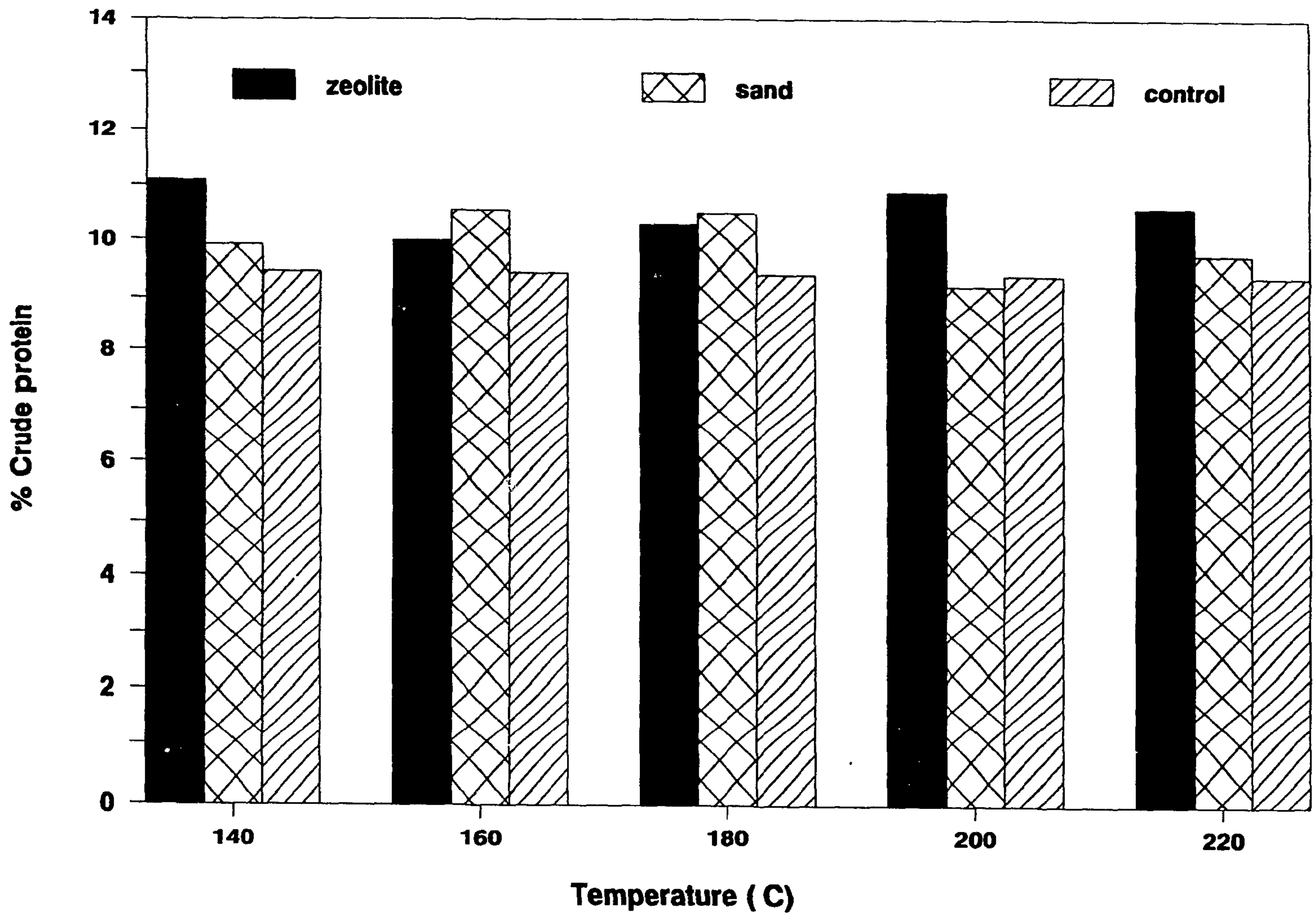


Fig. 7.1 Protein content of heat treated and untreated corn

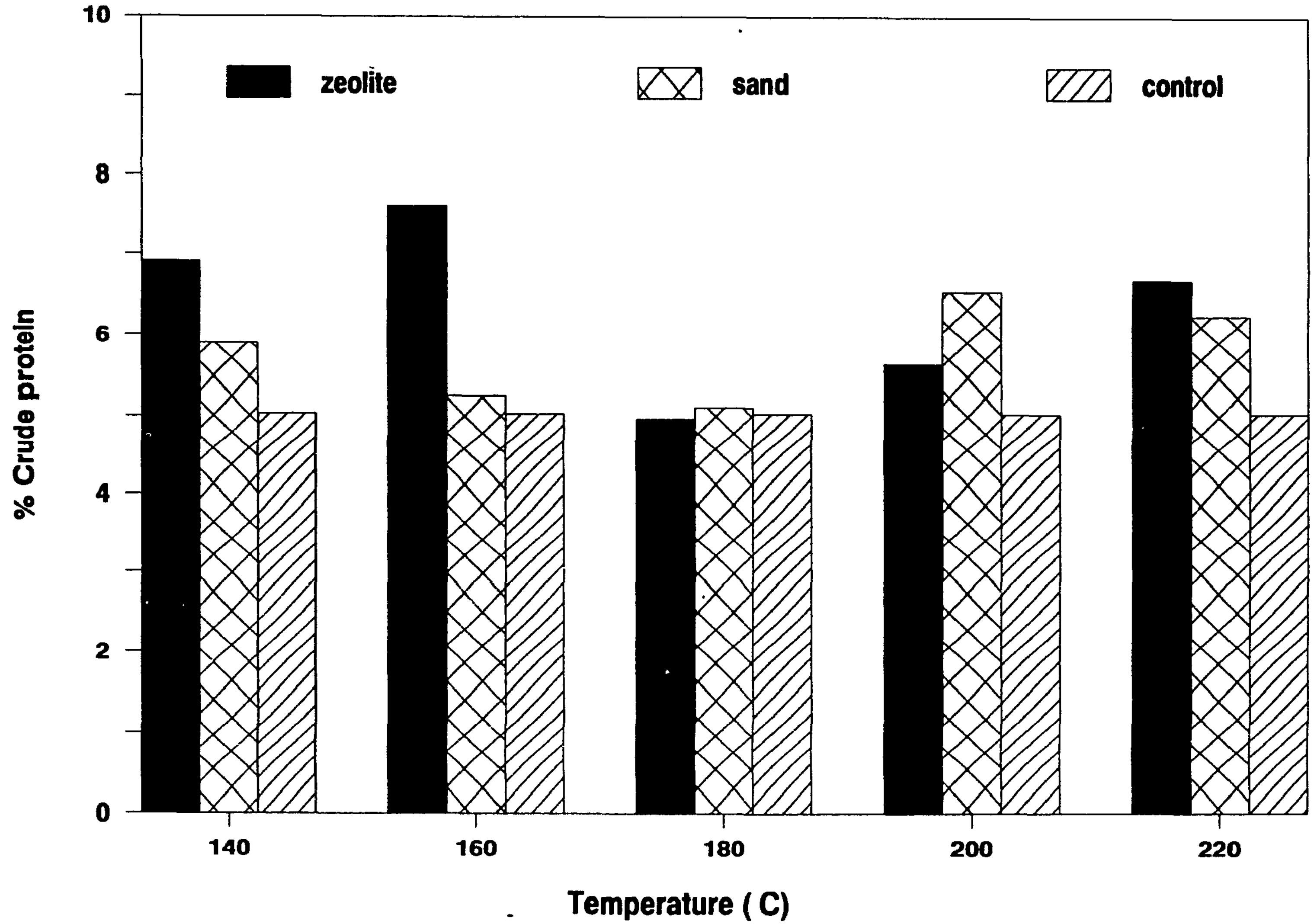


Fig. 7.2 Percentage protein in acid detergent fibre

Table 7.6. Results of acid detergent fibre analysis of corn processed for 1000 s

Medium	Medium Temp. (°C)	Dry Matter (%)	ADF (%)
	140	89.48	2.65
	160	89.74	3.15
Chabazite	180	89.81	3.81
	200	90.39	4.03
	220	89.87	3.81
	140	86.32	3.22
	160	89.51	3.33
Sand	180	89.36	3.85
	200	89.09	4.17
	220	89.30	3.26
Control		88.11	3.04

hygroscopic product than if dehydrated at a higher temperature. Therefore, the susceptibility of processed corn to moulds should be examined.

7.4 Other quality indices

One of the major concerns in using a solid particulate medium for grain drying is the possibility of contaminating grain. Accurate measurement of the amount of zeolite residue in corn is not practical because physical separation of the zeolite residue from the corn is fraught with difficulties. Zeolite has a very high ion exchange property. Samples of the corn processed with synthetic zeolite were tested to determine the amount of synthetic zeolite residue and, thus, the possible amount of aluminium. Spectrophotometer results indicated that the highest level of aluminium detected was 300 ppm. Valdivia et al. (1978) reported that dietary aluminium up to 1200 ppm does not have detrimental effects on experimental animals.

No tests were made for grain processed with the natural zeolite. The use of natural zeolites as dietary supplement was discussed in detail in Section 2.4.2. Therefore, it is unlikely that the minimal amount of the natural zeolite residue in the grain corn would have an unwholesome effect to the quality of processed corn as animal feed.

It may be asked how this method of drying will affect germination of the seed. The corn temperature in our experiments was in the range of 60 - 100°C, depending on the initial medium temperature and the residence time. Brooker et al. (1974) suggested that in order to avoid any reduction in germination, the drying temperature must be kept below 43°C (110°F) so it is obvious that grain processed by this method will not be fit for seed. However, it must be realized that no one method can be the panacea to all problems, and a new approach should be weighted against its own merits. Khan (1972) mentioned that "in the tropics, 98 percent of paddy grain is consumed as food and retention of seed viability assumes only minor importance." The same is true for corn, in the sense that only less than 0.5 percent of the total corn disappearance is for seed (Watson, 1988).

Another important physical change due to thermal processing is the formation of checks and cracks. It was observed that corn dried by the heated medium (molecular sieves or sand) at 250°C was swollen and cracked. The swelling effect for corn immersed in molecular sieves or sand with the initial temperature of 200°C depended on the MGMR. For the highest MGMR (8:1), checks were noticeable. Corn processed at 150°C did not show any visible signs of checks or cracks on the surface. Moreover, there was no evidence of cracks, checks, swelling, or change in colour for the corn mixed with the chabazite, where the MGMR was 3:1 and the initial medium temperature in the range of 140 - 220°C.

It was not practical to determine the damage due to thermal processing because there will be some degree of damage in combining the grain (or shelling it with a mechanical sheller). We did try to shell the corn manually but it was not practical to manually shell all the corn required in these experiments. Therefore, except for visual observation, the idea of any comprehensive test for physical damage to the grain was dropped.

7.5 Summary and conclusions

Naturally moist corn dried by mixing it with a heated bed of granular zeolite or sand was used for animal feed. The results of this study indicated that the drying of corn for 2 - 4 min with granular materials having an initial temperature of 150-250 °C would not adversely damage the nutritive quality of the grain.

Acid detergent fibre analysis indicated some damage to corn treated for 1000 s in a mixture with an initial temperature in the range of 140 - 220°C. However, similar to the animal feed study, the damage cannot be considered significant.

The results of atomic absorption spectrophotometry indicated only small amounts of molecular sieves residue on the processed grain. The highest amount of aluminium, as an indication of zeolite residue, was 300 ppm.

CHAPTER EIGHT

EPILOGUE

We should be careful to get out of an experience only the wisdom that is in it - and stop there; lest we be like the cat that sits down in a hot stove-lid. She will never sit down on a hot stove-lid again - and that is well; but she will never sit down on a cold one anymore — *Mark Twain* (Samuel Longhorn Clemens, 1835-1910)

8.1 Recapitulation of the conclusions

This study was directed at particulate medium drying. The conclusions drawn with regard to the different aspects of the process are summarized as follows:

1. Molecular sieves performed better than sand as a medium for drying corn.

2. The means of grain temperatures using the molecular sieves were significantly higher than those of sand; this could be attributed to a higher heat transfer coefficient between molecular sieves and grain than between sand and grain.

3. The relative humidity of the air in the dryer when using sand approached saturation rapidly (> 90 % for times of less than 2 min); RH using molecular sieves dropped with residence time until it reached a steady value of 10 - 20 percent.

4. With increased residence times, the difference between the MRP by the molecular sieves and sand increased. The mean MRP for the molecular sieves at the highest residence time, for all media temperatures, was about twice that achieved by sand.

5. The main resistance to moisture diffusion in grain zeolite mixtures came from the corn kernel. The diffusivity of moisture in the zeolite did not result in a bottleneck.

6. Luikov's model, which involves the coupling effect of heat and mass transfer, was solved numerically. The results show good agreement with experimental data for moisture sorption in corn-zeolite mixtures.

7. The change in the nutritive quality of corn due to thermal processing using heated granular zeolites as the solid particulate medium was not significant.

8. The amount of zeolite residue on the processed corn was not significant.

8.2 Contribution to knowledge

This thesis has made an original contribution to knowledge by providing information on aspects of the drying process using granular media that have not been studied by other researchers. The knowledge gained is of value from the point of view of application of engineering to agriculture as well as constituting original contribution to the science of engineering. More specifically, the contribution to knowledge can be summarized as follows:

1. This study demonstrates the possibility of accelerated drying of corn by mixing it with heated granular zeolite.

2. It is shown that the nutritive quality of corn is not significantly damaged by accelerated drying using zeolites.

3. The resistance to moisture diffusion in a grain-zeolite mixture is due mainly to that of corn; the diffusivity of moisture in zeolite does not introduce any bottleneck.

4. A mathematical model for simultaneous heat and mass transfer in corn-zeolite mixtures was numerically solved.

8.3 Recommendations for further studies

Faced with limited time and resources, researchers often wonder whether they should terminate the particular phase of research work. If they are lucky, they may continue the research work at a later time, or colleagues may pursue their goal.

In the course of this study, we have faced the following interesting research problems, which we bequeath as recommendations for further study.

1. In this study I repeatedly referred to the use of zeolites in animal nutrition, i.e. ingestion of zeolites. However, it was observed that a degree of dust will be generated during the drying process. Since occupational safety of workers must be of utmost concern to any project engineer, the health effect of zeolite dust due to inhalation would therefore need to be studied, if zeolite is used in a continuous drying process. Characterization of zeolite dust, the possibility of dust particles coagulating due to moisture, and the respirability of the dust should be studied. The diffusion of zeolite dust in the work area due to thermophoresis (thermal gradient) as well as deposition by convective diffusion could be an interesting problem to investigate.

2. The model dryer was designed and operated with the idea of adiabatic processing in mind. However, in the prototype there is a constant supply of heat through the innermost cone (combustion chamber) wall due to burning gas. The heat input term should therefore be considered in the theoretical model if the model results are to be compared with the experimental data from the prototype dryer. After measuring the temperature of the cone wall during the drying operation in the continuous dryer, a comparable steady temperature gradient should be applied in the model dryer as well. Consequently, the heat input term should be included in the theoretical model.

3. The main objective of drying cereal grains is to improve their storage life. Using a heated particulate medium for drying implies accelerated drying, which could enhance or deteriorate certain physical properties of the processed grain. It is imperative to conduct a comparative study of grain processed by the conventional method and using a particulate medium. Characterization of the physical attributes of these processed grains during handling and storage would be very useful.

4. Use of a two-stage drying process. In the first part, a medium such as sand would be used for heating the grain, while in the second zeolite to be mixed with the heated grain for moisture removal (adsorption). The zeolite should be at room temperature initially, since it is not to be used for heating the grain and only adsorption. Furthermore, by starting from a low temperature the adsorption capacity of zeolite will remain high. The saturated zeolite would not be regenerated by a thermal swing but rather by a pressure swing. Regeneration by a pressure swing is expected to result in a faster regeneration time and less aging of the zeolite due to heating. The efficiency and economic viability of a two-stage drying process should be compared with those of the single-stage thermal swing process used in this study.

REFERENCES

Aguilera, J.M.; Lusas, E.W.; Ubersax, M.A.; and Zabik, M.E., 1982.
Roasting of navy beans (*Phaseolus vulgaris*) by particle-to-particle heat transfer. J. Food Sci. 47:996-1000 and 1005.

Akpaetok, O.I., 1973.
Shelled corn drying with heated sand. M.S. Thesis, Univ. of Wisconsin.

AOAC, 1980.
Official methods of analysis of the Association of Official Analytical Chemists. 13th ed., Washington, 1018 pp.

Arboleda, J.R.; Manalo, A.S.; and Khan, A.U., 1973.
Accelerated drying of paddy.
Annales de technologie 22(3): 257-273.

ASAE, 1983.
Agricultural Engineers Yearbook of Standards.
American Society of Agricultural Engineers, St. Joseph, MI, 853 pp.

Bakker-Arkema, F.W.; Brook, R.C.; and Lerew, L.E., 1972.
Cereal grain drying. In: Advances in cereal Sci. and Tech. (Y. Pomeranz, ed.), Am. Soc. Cereal Chemists, St. Paul, MN, 2:1-90.

Barrer, R.M. and Fender, B.E.F., 1961
The diffusion and sorption of water in zeolites - II. Intrinsic and self-diffusion. J. Phys. Chem. Solids 21(1): 12-24.

Becker, H.A., and Sallans, H.R., 1955.
A study of internal moisture movement in the drying of the wheat kernel. Cereal Chem. 32 (3):212-226.

Bergles, A.E., 1978.
Enhancement of heat transfer. Proc. of the Sixth Int. Heat Transfer Conf., Toronto, 6:89-108.

Breck, D.W., 1980.
Molecular sieves. In: Kirk-Othmer Concise Encyc. of Chem. Tech. John Wiley and Sons, NY, pp. 772-774.

Breck, D.W. and Anderson, R.A., 1981.
Molecular sieves. In: Encyclopedia of chemical Technology. John Wiley and Sons, N.Y. 15: 638-669.

Breck, D.W. and Smith, J.V., 1959.
Molecular sieves, Sci. Am. 200(1):85-90,92 and 94.

Brooker, D.B.; Bakker-Arkema, F.W.; and Hall, C.W., 1974.
Drying of cereal grains. AVI Pub. Corp., Westport, CT, 265 p.

Cabell, C.A.; Davis, R.E. and Saul, R.A., 1958.
Some effects of variation in air drying temperature, heating time, air flow rate, and moisture content on nutritive value of field shelled corn.
J. Animal Sci. 17: 1204 (Abstract).

Carslaw, H.S. and Jaeger, J.S., 1959.
Conduction of heat in solids.
Oxford University Press, Second ed., 510 p.

Chancellor, W.J., 1968.
A simple grain drier using conducted heat.
Trans ASAE 11:857-862.

Chittenden, D.H. and Hustrulid, A., 1966.
Determining drying constants for shelled corn.
Trans ASAE 9:52-55.

Chung, D.S. and Fleske, L.F., 1973.
Development of a simple grain storage unit and method applicable to humid areas. Food and Feed Grain Institute, Kansas State Univ., Report No 37, 60 p.

Church, D.C., 1984.
Livestock feeds and feeding.
O & B Books, Inc., Second ed., Oregon, pp. 177-178,

Close, D.J. and Dankle, R.V., 1970.
Energy storage using desiccant beds. In: Proc. Int. Sol. Energy Soc. Conf., Melbourne, Australia, Paper No 7/24, 7 pp.

Clump, C.W., 1967.
Mixing of solids. In: Mixing theory and practice, U.W. Uhl and J.B. Gray (eds.), Academic Press, NY, pp. 263-286.

Crank, J., 1975
The mathematics of diffusion. Oxford U. Press, Oxford. 414 pp.

Danziger, M.T.; Steinberg, M.P.; and Nelson, A.I. 1972.
Drying field corn with silica gel.
Trans ASAE 15: 1071-1074.

Dietz, H.W., 1979.
Effective thermal conductivity of packed beds.
Ind. Eng. Chem. Fund. 18: 283-286.

Downs, H.W.; Kellerby, J.D.; Harper, J.M.; Haberstr ·h, D. and Marlatt, W.D., 1977.
Heat transfer by contact between agitated paracles.
Unpublished final report, Colorado State Univ., 89 p.

Emerick, R.J.; Carlson, C.W. and Winterfield, H.L., 1961.
Effect of heat drying upon the nutritive value of corn.
Poul. Sci. 40:991-994.

Farouk, S.M.; Brusewitz, G.H.; and Bloome, P.D., 1981.
Desiccant moisture sorption as altered by dust.
Trans ASAE 24 :1322-1325.

Finney, E.E., Mohsenin, N.N., and Hovanesian, J.D., 1963.
The thermal efficiency of conduction drying of shelled maize and the effect of temperature and kernel injury on the drying rate.
JAER 8: 62-69

Fisher, G.A., 1988.
Considering your crop options for 1988. Ontario Corn Producer 3(10):6.

Flanigan,E.M., 1984.
Adsorption properties of molecular sieve zeolites.
In: Zeo-Agriculture (W.G. Pond and F.A. Mumpton, eds.)
Eastview Press, Boulder, Colorado pp. 55-68.

Fortes, M. and, Okos M.R. 1981.
Non-equilibrium thermodynamics approach to heat and mass transfer in corn kernels. Trans. of ASAE. 24:761-769.

Foster, G.H., 1973.
Heated-air grain drying. In: Grain drying: Part of a system.
(R.N. Sinha and W.E. Muir, eds.), AVI Pub. Co., CT, pp. 189-208.

Furia, T.E. (ed.), 1980.
Regulatory status of direct food additives. CRC Press, Inc., Boca Raton, FL, p 247.

Garcia-Lopez, R.; Elias, A.; Pereze de la Paz, J.; and Gonzalez, G., 1988.
The utilization of zeolite by dairy cows. I. The effect on milk composition.
Cuban J. Agric. Sci. 22:33-38.

Goering, H.K. and van Soest, P.J., 1970.
Forage fiber analysis. USDA, Agricultural Handbook No 379, 20 p.

Gottardi, G., 1978.
Mineralogy and crystal chemistry of zeolites. In: Natural zeolites occurrence, properties, use. (L.B. Sand and F.A. Mumpton, eds.) Pergamon Press, Oxford, pp. 31-44.

Graham, V.A.; Bilanski, W.K.; and Menzies, D.R., 1983.
Adsorption grain drying using bentonite.
Trans ASAE 26: 1512-1515.

Graham, V.A. and Bilanski, W.K., 1986.
Simulation of grain drying in intimate contact with adsorbents.
Trans ASAE 29:1776-1783.

Gurr, C.G.; Marshall, T.J.; and Hutton, J.T. 1952.
Movement of water in soil due to a temperature gradient.
Soil Sci. 71 (5):335-345.

Hall, C.W., 1980.
Drying and storage of agricultural crops.
AVI Publishing Corp., Westport, CT, 381 p.

Hall, G.E. and Hall, C.W., 1961.
Drying shelled corn by conduction heating.
Agric. Eng. 42: 186-187, and 196.

Harakas, N.K., and Beatty, K.O., 1963.
Moving bed heat transfer: effect of interstitial gas with fine particles.
Chem. Eng. Symposium Series 59, No 41, pp. 122-128.

Harmathy, T.Z., 1969.
Simultaneous moisture and heat transfer in porous systems with particular reference to drying. Ind. Eng. Chem. Fund. 8(1):92-103.

Hatfield, E.E. and Wilson, W.M.D., 1973.
Effect of drying temperature and heat treatment on the nutritive value of corn.
In: Proc. of a Symp. on "Effect of processing on the nutritive value of feeds".
Nat. Acad. Sci., Washington, D.C., pp. 151 - 170.

Hathaway, I.L., Yung, F.D. and Kiesselbach, 1952.
The effect of drying temperature upon the nutritive value and commercial grade of corn. J. Animal Sci. 11:430-440.

Hawkins, D.B. 1984.
Occurrence and availability of natural zeolites. In: Zeo-Agriculture (W.G. Pond and F.A. Mumpton, eds.), Westview Press, CO, pp. 69-78.

Hearon, J.Z., 1950. Some cellular diffusion problems based on Onsager's generalization of Fick's law. Math. Biophys. Bull. 12: 135-159.

Hodge, J.E. 1982.
Food and feed uses of corn. In: CRC Handbook of processing and utilization in agriculture. (I.A. Wolff, ed.), CRC Press, FL, Vol 2, Part I, pp. 79-87.

Holt, A.D., 1960.
Continuous heat-processing of granular and/or powdered solids in dry-state fluidization. Presented at the Fourth National Heat Transfer Conference, AIChE-ASME, Baffalo, NY, Aug 14-17, 1960.

Hougen, O.A.; McCauley, H.J.; and Marshall, W.R., 1940.
Limitations of diffusion equation in drying.
Trans AIChE 36:183-209.

Hsiao, J.Y., 1974.
Application of silica gel for on-farm grain drying and storage in developing countries. MS Thesis, Kansas State U., 74 p.

Hussain, A.; Chen, C.S.; and Clayton, J.T., 1973. Simultaneous heat and mass diffusion in biological materials. J. Agric. Eng. Res. 18:34 -354.

Hussain, A.; Nelson, G.L.; and Clary, B.L., 1970. Evaluating thermodynamic parameters of moisture transfer in food products. ASAE Paper No 70-385.

Iengar, N.G.C.; Bhasker, R.; and Dharmarajan, P., 1971.
Studies on sand parboiling and drying of paddy.
J. Ind. Soc. Agric. Eng. 8:51-54.

Johnson, H.K. and Dale, A.C., 1954.
Heat required to vaporize moisture.
Agric. Eng. 35(10): 705-709 and 714.

Johnson, W.H. and Hassler F.J. 1968.
Steady-state thermodynamics: A methodology for agricultural process engineering. Trans. of ASAE. 11: 68-73.

Keey, R.B., 1972.
Drying principles and practice. Pergamon Press, Oxford, 358 p.

Kelly, C.F., 1939.
Methods for drying grain on the farm.
Agric. Eng. 20 (4) : 135-138.

Kersh, C.K., 1961.
Molecular sieves, Reinhold Pub. Corp., NY, 129 p.

Kerr, G.T., 1989.
Synthetic zeolites. Sci. Am. 261(1):100-105.

Khan, A.U., 1972.
Rice drying and processing equipment for Southeast Asia.
ASAE Paper No. 72-339.

Khan, A.U.; Amilhussin, A.; Arboleda, J.R.; Manola, A.S. and Chancellor, W.J., 1973.
Accelerated drying of rice using heat conducting media.
ASAE paper No 73-321.

Kramer, A. and Twigg, B.A., 1970.
Quality control for the food industry. AVI Pub. Co., CT, 1:10.

Kröll, K.; Mujumdar, A.S.; and Menon, A.S., 1980.
Drying since the millenniums. In Drying '80 (A.S. Mujumdar, ed.).
Hemisphere Pub. Corp., Washington, 2:485-494.

Kunii, D. and Smith, J.M., 1960.
Heat transfer characteristics of porous rocks. AIChE J. 6:71-78.

Kuprianoff, J., 1958.
'Bound water' in foods. In: Fundamental aspects of the dehydration of foodstuffs. Soc. of Chem. Ind., London, pp. 14-23.
J. Food Process Eng. 4:137-153.

Kuzmark, J.M. and Sereda, P.J., 1957. The mechanism by which water moves through a porous material subjected to a temperature gradient: I. Introduction of a vapor gap into a saturated system. Soil Sci. 84: 291-299.

Lapp, H.M.; Mittal, G.S. and Townsend, J.S., 1977.
Drying wheat with heated sand.
CSAE paper no. 77-105.

Lapp, H.M. and Manchur, L.R., 1974.
Drying oilseeds with a solid heat transfer medium.
CSAE Paper No. 74-504.

Lewis, W.K., 1921.
The rate of drying of solid materials. J. Ind. Eng. Chem. 13:427-432.

Luikov, A.V., (Also transliterated Lykow, A.W.), 1966.
Heat and mass transfer in capillary porous bodies.
Pergamon Press, Oxford, 523 p.

Luikov, A.V. and Mikhailov, U.A., 1961.
Theory of energy and mass transfer. Prentice-Hall, Inc., NY, 324 p.

Luikov, A.V.; Shashkov, A.G.; Lasiliev, L.L.; and Fraiman, Yu. E., 1968.
Thermal conductivity of porous systems.
Int. J. Heat Mass Transfer 11: 117-140.

Luikov, A.V., 1968.
Analytical Heat diffusion theory. Academic Press, NY, 685 p.

Ma, C.-S.; Yong, S.-K; Tzeng, C.-M;and Wu, H.-K, 1984.
Effect of feeding clinoptilolite on embryo survival in swine.
In: Zeo-Agriculture, pp. 151-156.

Madhusudana, C.V. and Fletcher, L.S., 1986.
Contact heat transfer - The last decade.
Am. Inst. of Aeronautics and Astronautics J. 24:510-523.

Maxwell, J.C., 1892.
A treatise on electricity and magnetism, Oxford U. Press, 3rd ed.,
Vol 1, pp. 440-441.

Meiring, A.G.; Bakker-Arkema, F.W.; and Raschke, K., 1971.
Simultaneous heat and mass transfer of small grains.
ASAE Paper No 71-819.

Meredith, R.E. and Tobias, C.W., 1960.
Resistance to potential flow through a cubical array of spheres.
J. Appl. Physics 31:1270-1273.

Miller, W.M., 1984.
Solid desiccants for food drying and energy storage.
ASAE Paper No. 84-6005.

Mittal, G.S.; Lapp, H.M.; and Townsend, J.S., 1985.
Feasibility of drying wheat with various solid heat transfer media.
Can. Agric. Eng. 27 (2): 121-125.

Mohsenin, N.N., 1986.
Physical properties of plant and animal materials.
Gordon and Breach Sci. Publishers, NY, 891 p.

Mumpton, F.A., 1978.
Natural zeolites : A new industrial mineral commodity. In: Natural zeolites,
Occurrence, properties, use. (L.B. Sand and F.A. MUmpton, eds.),
Pergamon Press, Oxford, pp 3-27.

Mumpton, F.A., 1984a.
Natural zeolites. In: Zeo-Agriculture, pp 33-34.

Mumpton, F.A., 1984b.
Flammae et Fumus Proximi Sunt: The role of natural zeolites in agriculture and
aquaculture. In: Zeo-Agriculture, pp 3-27.

Mumpton, F.A. and Fishman, P.H., 1977.
The application of natural zeolites in animal science and aquaculture.
J. Animal Sci. 45:1186-1203.

Nestrov, N. 1984.
Possible applications of natural zeolites in animal husbandry.
In: Zeo-Agriculture, pp. 163-169.

Newman, A.B., 1931a.
The drying of porous solids: diffusion and surface emission equations.
Trans AIChE 27: 203-220.

Newman, A.B., 1931b.
The drying of porous solids: Diffusion calculations.
Trans AIChE 27: 310-333.

O'Neill, 1966.
Measurement of specific heat functions by differntial scanning calorimeter.
Anal. Chem. 38(10):1331-1336.

Onsager, L. 1931.
Reciprocal relations in irreversible processes.
Physical Review, Part I. 37: 405-426, Part II. 38:2265-2279.

Oxley, T.A., 1948.
The scientific principles of grain storage. Northern Pub. Co., Ltd., Liverpool, 103 p.

Özisik, M.N., 1980.
Heat conduction. John Wiley and Sons, NY, 687 p.

Özisik, M.N., 1977. Basic Heat Transfer. McGraw-Hill Kogakusha, Ltd., Tokyo, 572 p.

Özisik, M.N., 1968.
Boundary value problem of heat conduction.
International Textbook Co., PA, 505 p.

Pabis, S. and Henderson, S.M., 1961.
Grain drying theory. II. A critical analysis of the drying curve for shelled maize. J. Agric. Eng. Res. 6: 272-277.

Pannu, K.S. and Raghavan, G.S.V., 1987.
A continuous flow particulate medium grain processor.
Can. Agric. Eng. 29:39-43.

Peart, R.M. and Lien, R.M., 1975.
Grain drying energy requirement. ASAE Paper No 75-3019.

Philip, J.R. and De Vries, D.A., 1957.
Moisture movement in porous materials under temperature gradients.
Trans Am Geophys. Union 38(8):222-232.

Raetskaya, I.V. 1987.
[The use of zeolites in feeding of farm animals.]
Nutrition Abs. and Rev. (Ser. B) 57(6):346, C.A.B., UK.

Raghavan, G.S.V., 1973.
Heat transfer studies using granular media.
PhD Thesis, University of Colorado.

Raghavan, G.S.V. and Harper, J.M., 1974.
High temperature drying using a heated bed of granular salt.
Trans ASAE 17:108-111.

Rao, S.M. and Toor, H.L., 1984.
Heat transfer between particles in packed beds.
Ind. Eng. Chem. Fundam. 23: 294-298.

Rao, M.S. and Toor, H.L., 1987.
Heat transfer from a particle to a surrounding bed of particles. Effect of size and conductivity ratio. Ind. Eng. Chem. Res. 26:469-474.

Rayleigh, L., 1892.
On the influence of obstacles arranged in rectangular order upon the properties of a medium. Philosoph. Mag. and J. of Sci., Ser. 5, 34:481-502.

Richard, P. and Raghavan, G.S.V., 1980.
Heat transfer between flowing granular materials and immersed objects.
Trans ASAE 23 (6) : 1564-1568, and 1572.

Rossen, J.L. and Hayakawa, K., 1977. Simultaneous heat and moisture transfer in dehydrated food: A review of theoretical models. In: Water removal processes: drying and concentration of food and other materials.
AIChE Symp. Ser. No. 163, 73:71-78.

Russell, H.W., 1935.
Principles of heat flow in porous insulators. J. Am. Ceramic Soc. 18:1-5.

Rutgers, R., 1965.
Longitudinal mixing of granular materials flowing through a rotary cylinder.
Chem. Eng. Sci. 20: 1079-1087.

Ruthven, D.M., 1984.
Principles of adsorption and adsorption processes.
John Wiley and Sons, NY, 433 p.

Saravacos, G.D., and Raouzeos, G.S., 1986.
Diffusivity of moisture in air-drying of raisins.
In : Drying '86. (A.S. Mujumdar, ed.), Hemisphere Pub. Corp.
Washington, 2:487-491.

SAS Institute, 1985.
Statistical Analysis system package. SAS Institute Inc., SAS Circle, PO Box 8000, Cary, NC.

Schiesser, W.E., 1977.
An introduction to the numerical method of lines integration of Partial Differential Equations. Lehigh Univ., PA, 97 p.

Schlünder, E.U., 1981.
Heat transfer between packed beds, agitated and fluidized beds and submerged surfaces. In: Heat exchangers: Thermal-hydraulic fundamentals and design, (S. Kakac; A.E. Bergles; and F. Mayinger, eds.), Hemisphere Pub. Corp., Washington, pp. 177-208.

Schlünder, E.U., 1982.
Particle heat transfer.
Proc. of the Seventh Int. Heat Transfer Conf., Hemisphere Pub. Corp., Washington, 1:195-211.

Schuepp, P.H., 1990.
Personal communication.
Department of Renewable Resources, Macdonald College of McGill University, Ste-Anne-de Bellevue, PQ, Canada H9X 1C0.

Shabanov, S.I., 1963.
An analytical investigation of the heating of a granular material mixed with a solid heat-transfer medium. Int. Chem. Eng. 3:225-228.

Sherwood, T.K., 1929. The drying of solids. Ind. Eng. Chem. Part I. 21: 12-16, Part II. 21: 976-980.

Shove, G.C., 1970.
Harvesting, conditioning and storage. In: Corn: culture, processing, products, G.E. Inglett (ed.), pp. 60-72, AVI Pub. Co., Westport, CT.

Sibley, K.J. and Raghavan, G.S.V., 1985.
Parameters affecting grain drying by immersion in a hot particulate medium. Drying Tech. 3 (1) : 75-99.

Sibley, K.J. and Raghavan, G.S.V., 1986.
Surface heat transfer coefficients for corn immersed in a granular bed. In: drying of solids (A.S. Mujumdar, ed.), Wiley Eastern Ltd., New Delhi, pp. 279-290.

Simonton, W. and Stone, M., 1985.
A counterflow particle-to-particle heat exchanger for thermal processing disinfection. ASAE Paper No 85-3009.

Sincovec, R.F. and Madsen, N.K., 1975.
Algorithm 494. PDEONE, Solutions of systems of partial differential equations. ACM Trans on Math. Software 1:261-263.

Singer, C.; Holymard, E.J.; and Hall, A.R., (eds.), 1958.
A history of technology. Oxford U. Press, Vol 1, p 264.

Statistics Canada, 1983.
Farm energy use 1981. Catalog No 21-519, Ministry of Supply and Services, Ottawa, 80 p.

Sturton, S.L.; Bilanski, W.K. and Menzies, D.R., 1983.
Moisture exchange between corn and the desiccant bentonite in an intimate mixture. Can. Agric. Eng. 23(1): 139-141.

Sullivan, W.N., and Sabersky, R.H., 1975.
Heat transfer to flowing granular media.
Int. J. Heat Mass Transfer 18 : 97-107.

Sullivan, J.E.; Costa,P.M.; Owen, F.N.; Jensen, A.H.; Wikoff, K.E.; and Hatfield, E.E., 1975. The effect of heat on the nutritional value of corn. In: Corn quality in world markets (L.D. Hill, ed.), The Interstate printers and publishers, Danville, Ill., pp. 45-63.

Sweeny, T.F.; Cervantes, A.; Bull, L.S.; and Hemken, R.W., 1984.
Effect of dietary clinoptilolite on digestion and rumen fertilization in steers. In: Zeo-Agriculture pp. 177-187.

Syarief, A.M.; Gustafson, R.J; and Morey, R.V., 1987.
Moisture diffusion coefficient for yellow dent corn. Trans ASAE 30: 522-528.

Tessier, S. and Raghavan, G.S.V., 1984.
Heat transfer by mixing in solid media with a flighted rotating drum.
Trans ASAE 1233-1238.

Union Carbide, 183.
Molecular sieves catalogue. Union Carbide Corp., CT, 19 pp.

Valdivia, R.; Ammerman, C.B.; Wilcox, C.J.; and Henry, P.R., 1978.
Effect of dietary aluminium on animal performance and tissue mineral levels in growing steers. J. Animal Sci. 47:1351-56

Vrzgula, L. and Bartko, P., 1984.
Effect of clinoptilolite on weight gain and some physiological parameters of swine. In: Zeo-Agriculture, pp. 157-162.

Watson, S.A. 1982.
Corn: Amazing maize. General properties. In: CRC Handbook of Processing and utilization. (I.A. Wolff, ed.), CRC Press, FL, Vol 2, Part 1, pp. 3-29.

Watson, S.A., 1988.
Corn marketing, processing, and utilization. In: Corn and corn improvement. (G.F. Sprague and J.W. Dudley, eds.), Am Soc Agron, No 18, Madison. WI, pp. 881-940.

White, J.L. and Ohlrogge, A.J., 1974.
Ion exchange materials to increase consumption of non-protein nitrogen by ruminants. Canadian Patent No 939186.

Young, J.H. and Whitaker, T.B., 1971. Numerical analysis of vapor diffusion in a porous composite sphere with concentric shells. Trans ASAE 14: 1051-1057.

APPENDICES

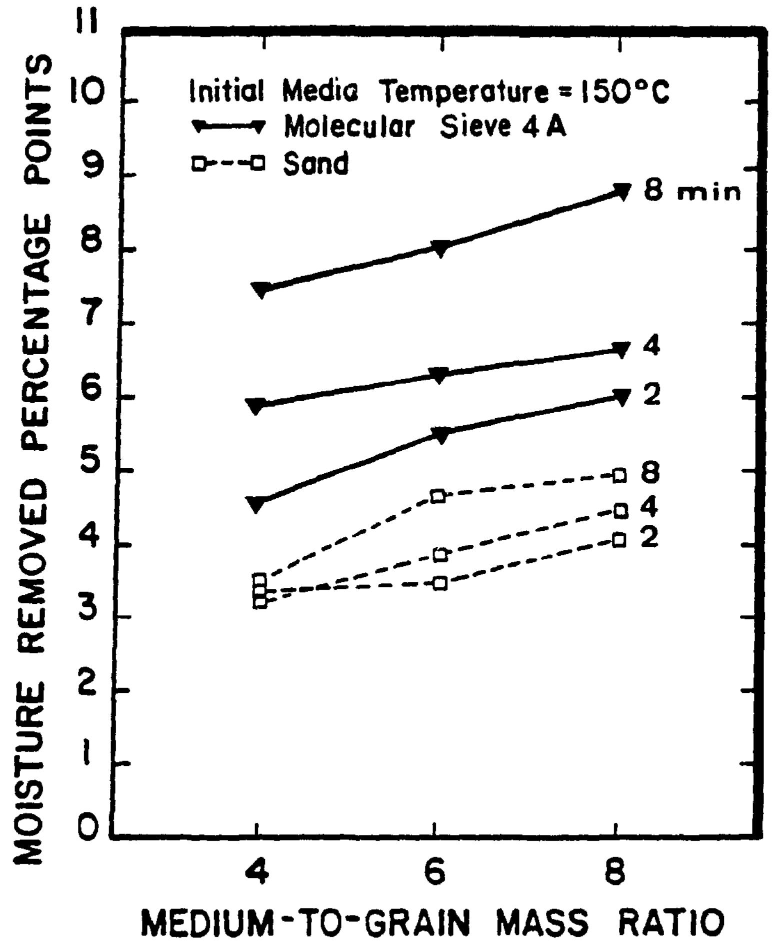


Fig. A1. Moisture removed with media at initial temperature of 150 °C

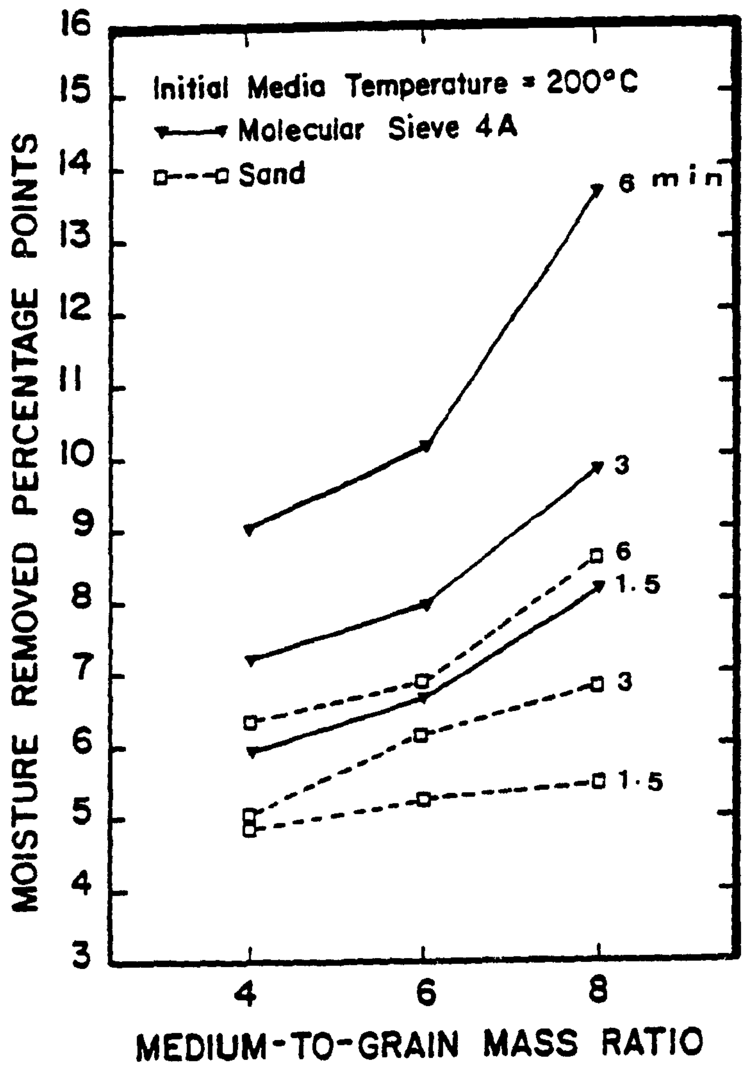


Fig. A2. Moisture removed with media at initial temperature of 200 °C

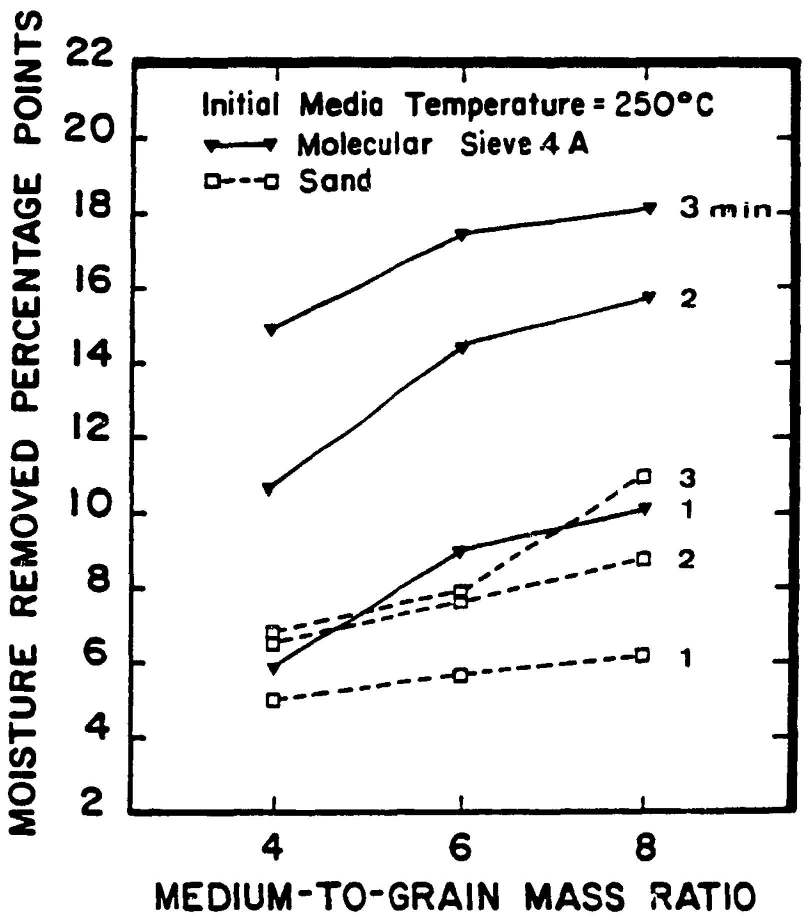


Fig. A3. Moisture removed with media at initial temperature of 250 °C

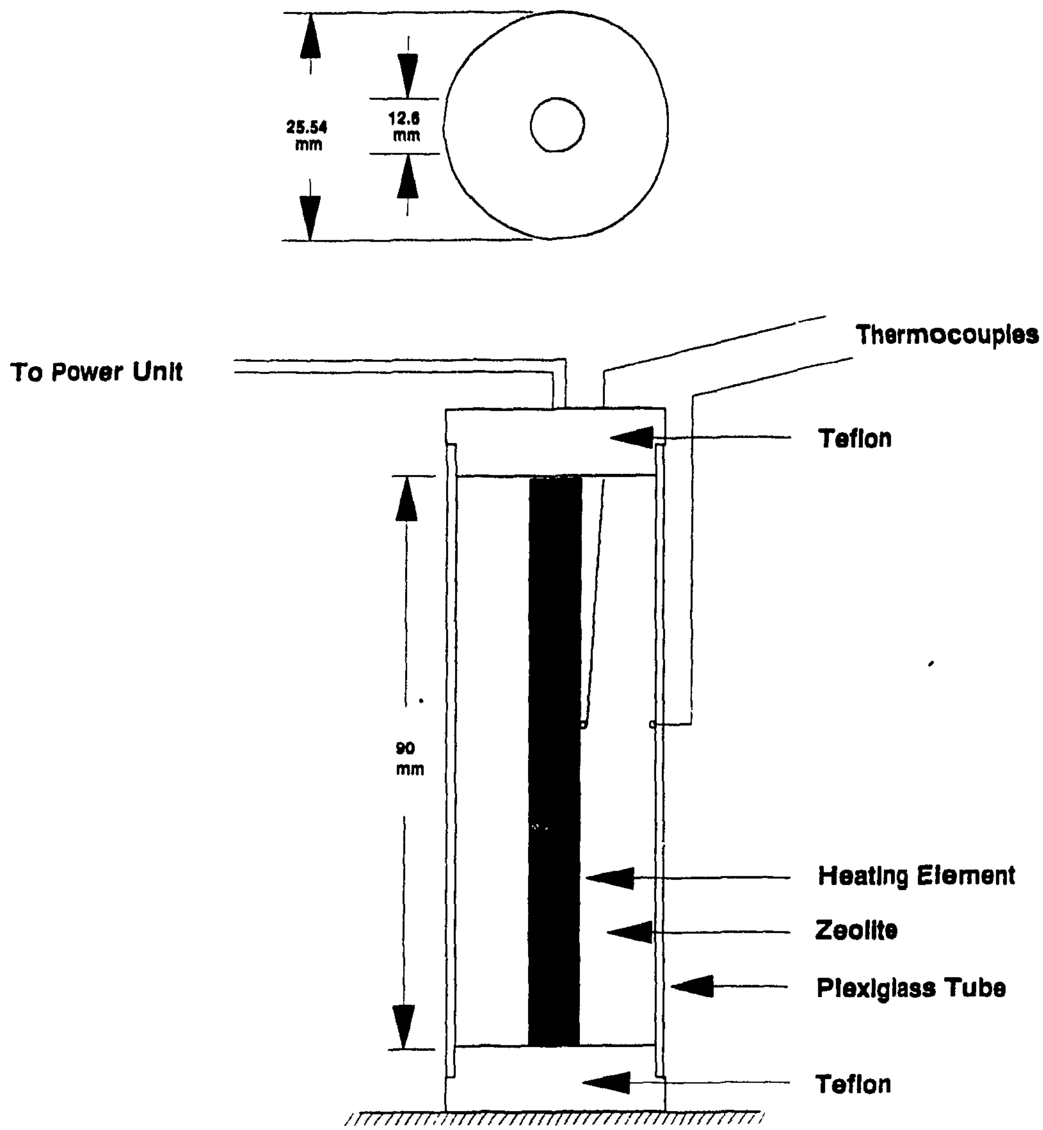


Fig. B1. Schematic diagram of the thermal conductivity apparatus

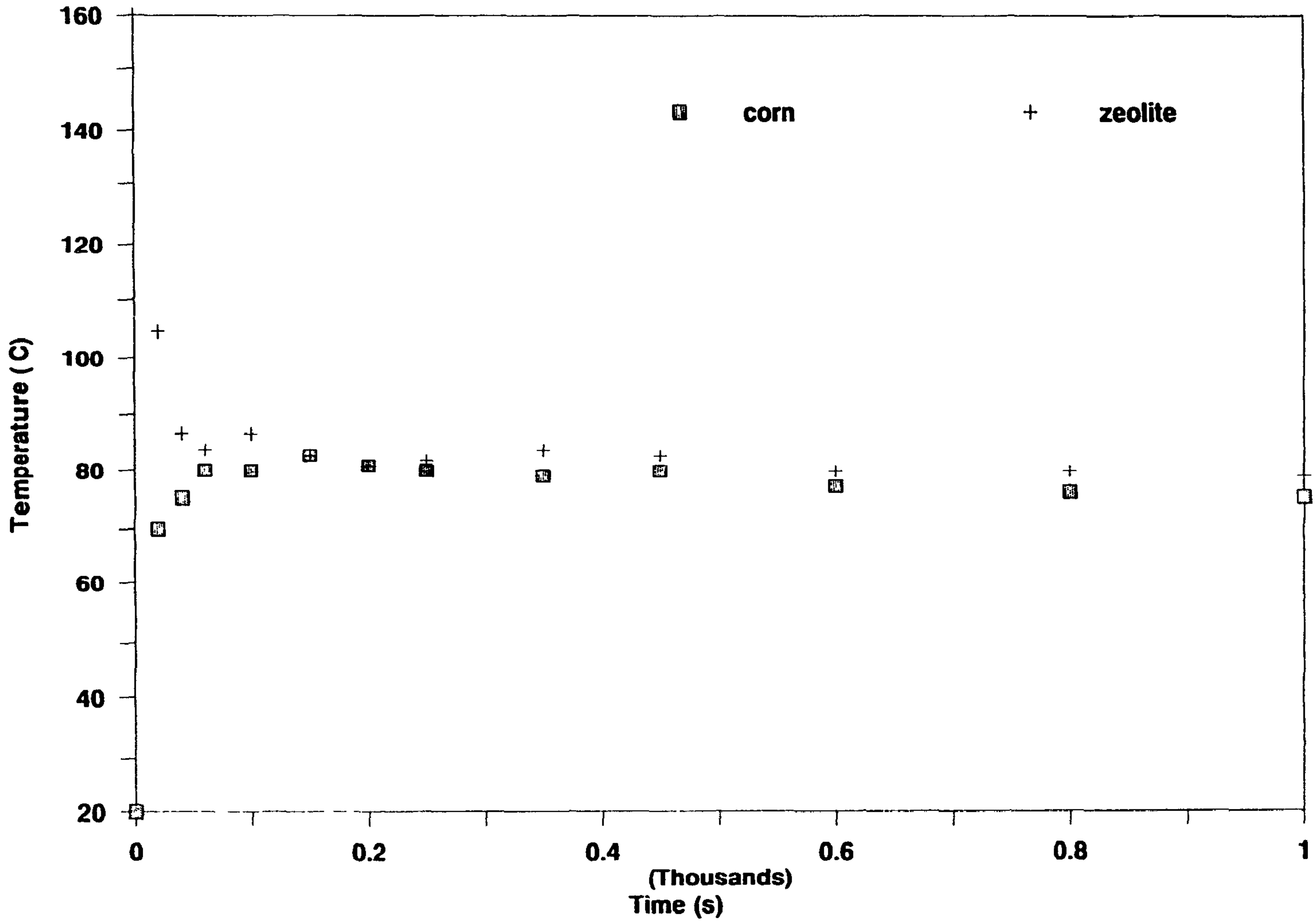


Fig. C1. Surface temperatures of corn and zeolite after mixing

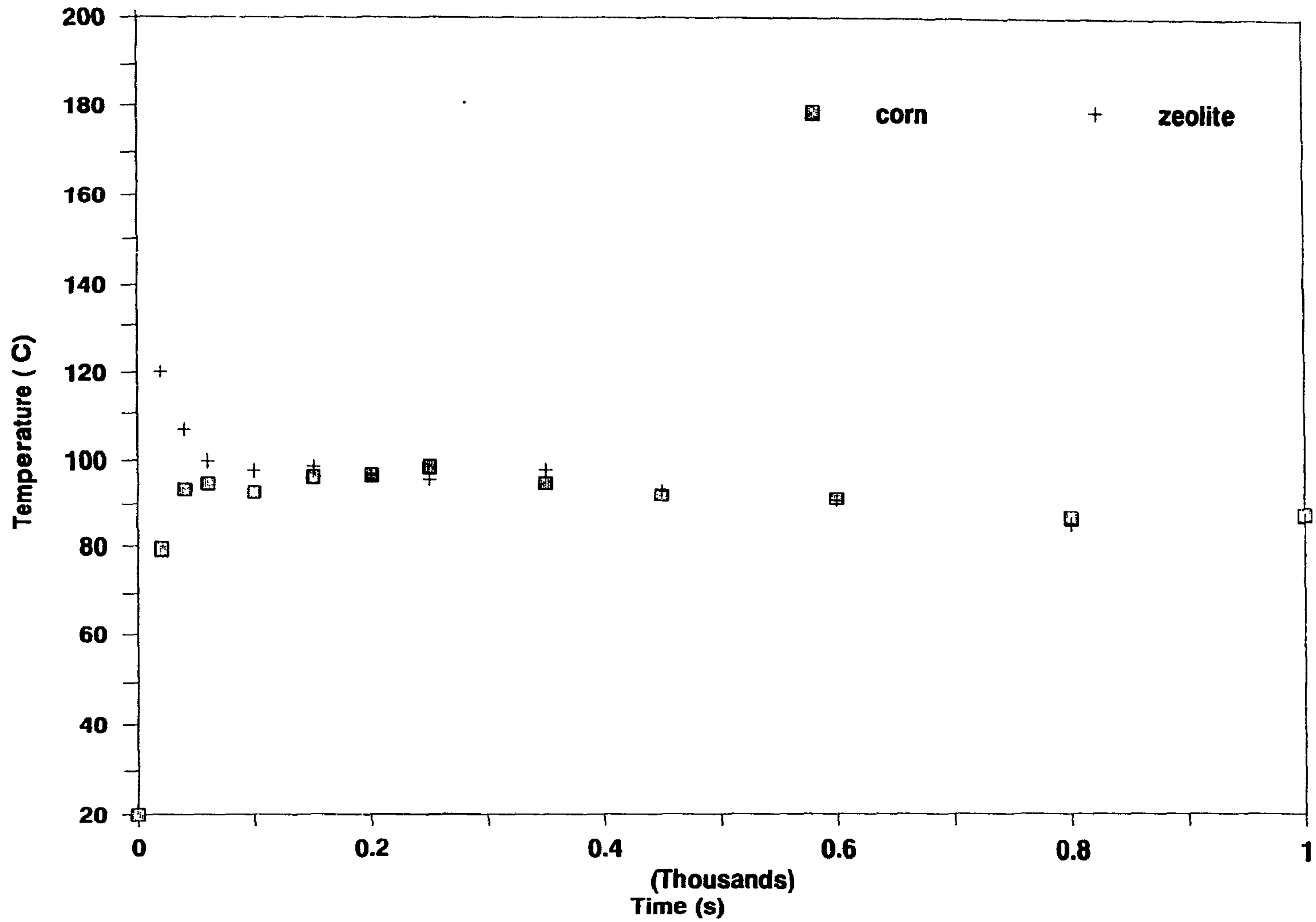
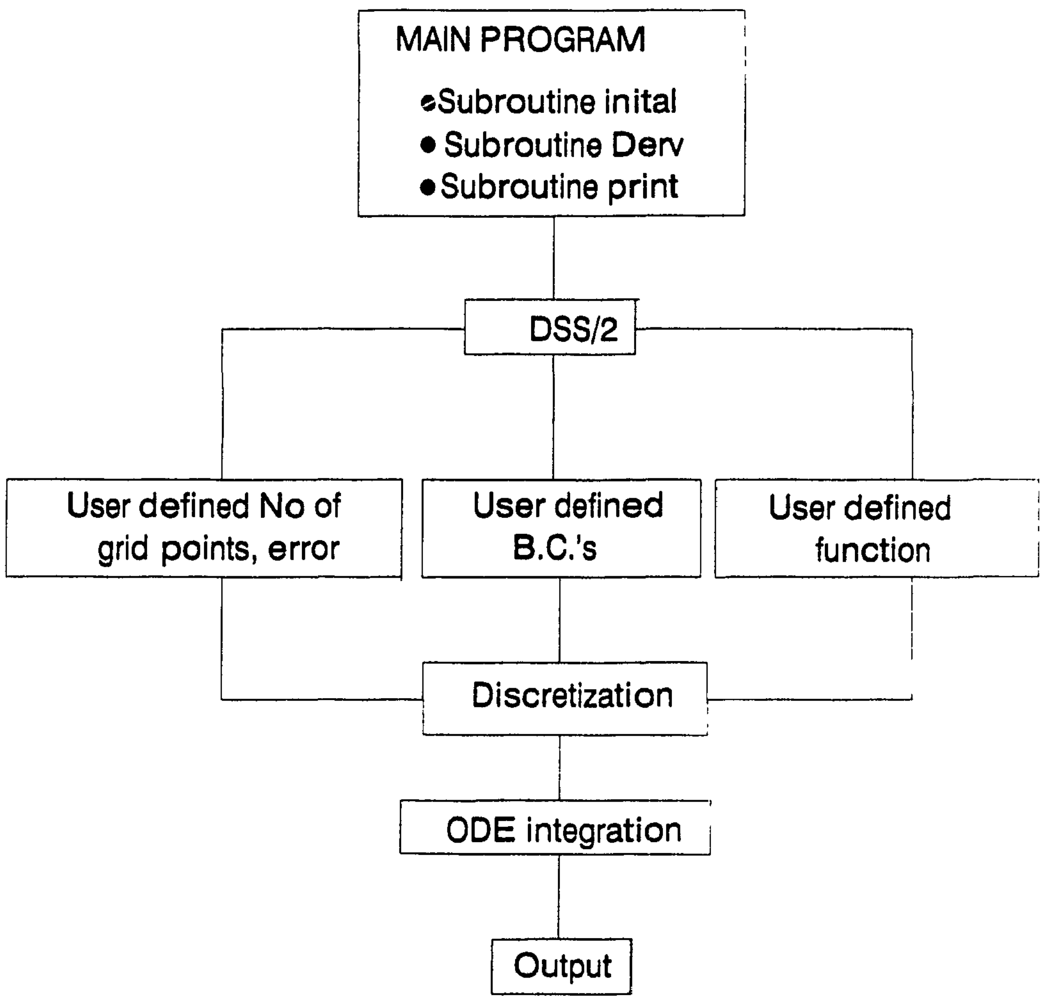


Fig. C2. Corn and zeolite surface temperatures after mixing

Appendix D1. Structure of the NMOL computer program



Appendix D2. Source code for the NMOL computer program

```
C       Coupled at the Boundary Heat and Mass Transfer
C
C       Application of Luikov's model for simultaneous Heat and Mass transfer
C       to Corn-Zeolite Mixtures
C
C       Filename NMr1.FOR
C
        SUBROUTINE INITAL
        implicit real*8(a-h,o-z)
        COMMON /T/T/Y/TC(31),TZ(31),UC(31),UZ(31)
       & /F/TCT(31),TZT(31),UCT(31),UZT(31)
       & /SD/TCR(31),TCRR(31),TZR(31),TZRR(31),
       & UCR(31),UCRR(31),UZR(31),UZRR(31)
       & /PARM/ALPHAC,ALPHAZ,AMDAC,AMDAZ,DC,DO,DZ,
       & TCO,TZO,N,R1,R2,Hc,Hz,Cpc,Cpz,H,TCONST
C
        OPEN(UNIT=8, FILE='OUT', STATUS='Unknown')
C
        TCO = 20.0D0
        TZO = 200.0D0
        UCO =0.40D0
        UZO =0.04D0
C
        DO 10 I =1, 31
        TC(I) = TCO
   10   CONTINUE
        DO 15 I =1, 31
        TZ(I) = TZO
   15   CONTINUE
        DO 20 I =1, 31
        UC(I)=UCO
   20   CONTINUE
        DO 25 I =1, 31
        UZ(I)=UZO
   25   CONTINUE
C
        ALPHAC = 0.001D0
        ALPHAZ = 0.025D0
        AMDAC = 0.00173D0
        AMDAZ = 0.015D0
        Cpc= 2.1D0
        Cpz= 0.724D0
        DC = 1.00D-05
        DO = 1.50D-05
        DZ = 5.08D-05
        H  = 0.032D0
        Hc = 2.326D03
```

```
      Hz = 1.6D03
      R1 = 0.4D0
      R2 = 0.6D0
      TCONST = 1.75665D0
C     TCONST = E/R, the time constant in the Arrhenius relation
      RETURN
      END
C ---------------------------------------------
      SUBROUTINE DERV
      implicit real*8(a-h,o-z)
      COMMON /T/T/Y/TC(31),TZ(31),UC(31),UZ(31)
     & /F/TCT(31),TZT(31),UCT(31),UZT(31)
     & /SD/TCR(31),TCRR(31),TZR(31),TZRR(31),
     &  UCR(31),UCRR(31),UZR(31),UZRR(31)
     & /PARM/ALPHAC,ALPHAZ,AMDAC,AMDAZ,DC,DO,DZ,
     &  TCO,TZO,N,R1,R2,Hc,Hz,Cpc,Cpz,H,TCONST
C
      IF(T.GT.20.D0) THEN
            Dc = 1.012D-05
              ELSEIF(T.GT.200.D0) THEN
            Dz = 0.90D-05
      ENDIF
C
      IF(T.GT.5.D0) THEN
            H = 0.00426D0*(T)**(-0.4076D0)
      ENDIF
C
      Dz = DO*DEXP(-TCONST * T)
C
      Uz(1) = Uc(31)
C
      CALL DSS004 (0.0D0,R1,31,TC,TCR)
C
      CALL DSS004 (0.0D0,R1,31,UC,UCR)
C
      CALL DSS004 (R1,R2,31,TZ,TZR)
C
      CALL DSS004 (R1,R2,31,UZ,UZR)
C
      TcR(1) = 0.0D0
      TzR(31)= 0.0D0
C
      UcR(1) = 0.0D0
      UzR(31)= 0.0D0
C
      TzR(1) = AMDAc/AMDAz*TcR(31)
      TcR(31)= H/AMDAc*(Tz(1)-Tc(31))
C
      UcR(31) = Dz/Dc*UzR(1)
```

```
C
      CALL DSS004 (0.0D0,R1,31,TCR,TCRR)
C
      CALL DSS004 (0.0D0,R1,31,UCR,UCRR)
C
      CALL DSS004 (R1,R2,31,TZR,TZRR)
C
      CALL DSS004 (R1,R2,31,UZR,UZRR)
C
      DO 35 I = 2, 31
            R = (dble(float(i-1))/(dble(float(30))))*R1
            UCT(I) = DC*(2.0d0/R*UCR(I) + UCRR(I))
35    CONTINUE
      UCT(1) = DC * (3.0D0*UCRR(1))
C
      DO 30 I = 2, 31
            R = (dble(float(i-1))/(dble(float(30))))*R1
            TCT(I) = ALPHAC*(2.0d0/R*TCR(I) + TCRR(I))
     &                                    + 0.5d0*Hc/Cpc*UCT(i)
30    CONTINUE
      TCT(1) = ALPHAC * (3.0D0*TCRR(1))
C
      DO 45 I = 2, 31
            R = (dble(float(i-1))/(dble(float(30))))*(R2-R1) + R1
            UZT(I) = DZ*(2.0D0/R*UZR(I) + UZRR(I))
45    CONTINUE
C
      UZT(1) = DZ * (3.0D0*UZRR(1))
C
      DO 40 I = 2, 31
            R = (dble(float(i-1))/(dble(float(30))))*(R2-R1) + R1
            TZT(I) = ALPHAZ*(2.0D0/R*TZR(I) + TZRR(I))
     &                                    + Hz/Cpz*UZT(I)
40    CONTINUE
C
      TZT(1) = ALPHAZ * (3.0D0*TZRR(1))
      RETURN
      END
C -----------------------------
      SUBROUTINE PRINT(NI,NO)
      implicit real*8(a-h,o-z)
      COMMON /T/T/Y/TC(31),TZ(31),UC(31),UZ(31)
     & /F/TCT(31),TZT(31),UCT(31),UZT(31)
     & /SD/TCR(31),TCRR(31),TZR(31),TZRR(31),
     & UCR(31),UCRR(31),UZR(31),UZRR(31)
     & /PARM/ALPHAC,ALPHAZ,AMDAC,AMDAZ,DC,DO,DZ,
     & TCO,TZO,N,R1,R2,Hc,Hz,Cpc,Cpz,H,TCONST
C
```

```
      WRITE(6,55) T
   55 FORMAT(' ','      TIME = ' ,D12.5)
      WRITE(6,60) (TC(I),I=1,31)
      WRITE(6,60) (TZ(I),I=1,31)
      WRITE(6,60) (UC(I),I=1,31)
      WRITE(6,60) (UZ(I),I=1,31)
   60 FORMAT('0',6D12.5)
C
      WRITE(8,65)T
   65 FORMAT(' ',' T=',D12.5)
      WRITE(8,70)(TC(I),I=1,31)
      WRITE(8,70)(TZ(I),I=1,31)
      WRITE(8,70)(UC(I),I=1,31)
      WRITE(8,70)(UZ(I),I=1,31)
   70 FORMAT('0',D12.5)
C
      WRITE(NO,75)T
   75 FORMAT(' ','T=',D12.5)
      WRITE(NO,80)(TC(I),I=1,31)
      WRITE(NO,80)(TZ(I),I=1,31)
      WRITE(NO,80)(UC(I),I=1,31)
      WRITE(NO,80)(UZ(I),I=1,31)
   80 FORMAT('0',6D12.5)
      RETURN
      END
```

Appendix D3. Source code for the BASIC computer program

```
5 'This program is written in BASIC version A3.30, 1987
7 ' Program to simulate heat transfer
10 ' between granular zeolite and a corn kernel immersed in it
15 ' written by: Dr P.H. Schuepp, Dept. of Renewable Resources
17 ' Macdonald College of McGill University, Ste-Anne-de Bellevue, PQ, Canada H9X 1C0
18 ' January 1990
20 REM
30 KEY OFF
40 DIM X(60),V(60),A(60),T(60),HC(60),NE(60),XX(60)
50 INPUT "TIME STEP"; H
60 INPUT "NO. OF ITERATIONS PER PROFILE";NN
65 INPUT "Enter Absolute time in sec for simulation";ABST
70 CLS
90 OPEN "dat" FOR OUTPUT AS #1
100 N = 0:NT=0
110 FOR I = 1 TO 60: X(I)=.01*I: V(I)=(4*3.14159/3)*(X(I)^3-X(I-1)^3):
        A(I) = 4*3.14159*X(I)^2:NEXT I
120 FOR I = 1 TO 40: T(I) = 20: NEXT I
130 FOR I = 41 TO 60: T(I) = 200: NEXT I
140 TI=(.01*T(41)+.34*T(40))/.35
150 FOR I = 1 TO 40: HC(I)=V(I)*1.7: NEXT I
160 FOR I = 41 TO 60: HC(I)=V(I)*.6: NEXT I
200 REM ENERGY BALANCE
205 IF TT>ABST GOTO 500
210 NE(1)=(T(2)-T(1))*.0017*A(1)/.01
220 FOR I = 2 TO 39: NE(I)=((T(I+1)-T(I))*A(I)-(T(I)-T(I-1))*A(I-1))*.0017/.01: NEXT I
230 NE(40)=((TI-T(40))*2*A(40)-(T(40)-T(39))*A(39))*.0017/.01
240 NE(41)=(T(42)-T(41))*.015*A(41)/.01-(.01*(T(41)-TI)*A(40))
250 FOR I = 42 TO 59: NE(I)=((T(I+1)-T(I))*A(I)-(T(I)-T(I-1))*A(I-1))*.015/.01: NEXT I
260 NE(60)=-(T(60)-T(59))*.015*A(59)/.01
280 REM
300 REM NEW TEMPERATURES
305 REM
310 FOR I = 1 TO 60: T(I)=T(I)+(NE(I)/HC(I))*H: NEXT I
320 TI = (.01*T(41)+.34*T(40))/.35
350 N=N+1:NT=NT+1:TT=NT*H:IF N<NN GOTO 210
380 SCREEN 1,0: COLOR 12,1
382 LINE (0,180)-(320,180),2
384 FOR I = 2 TO 60: LINE ((I-1)*5,180-(T(I-1)-20))-(I*5,180-(T(I)-20)),1: NEXT I
400 N=0: GOTO 200
500 CLOSE #1
600 END
```

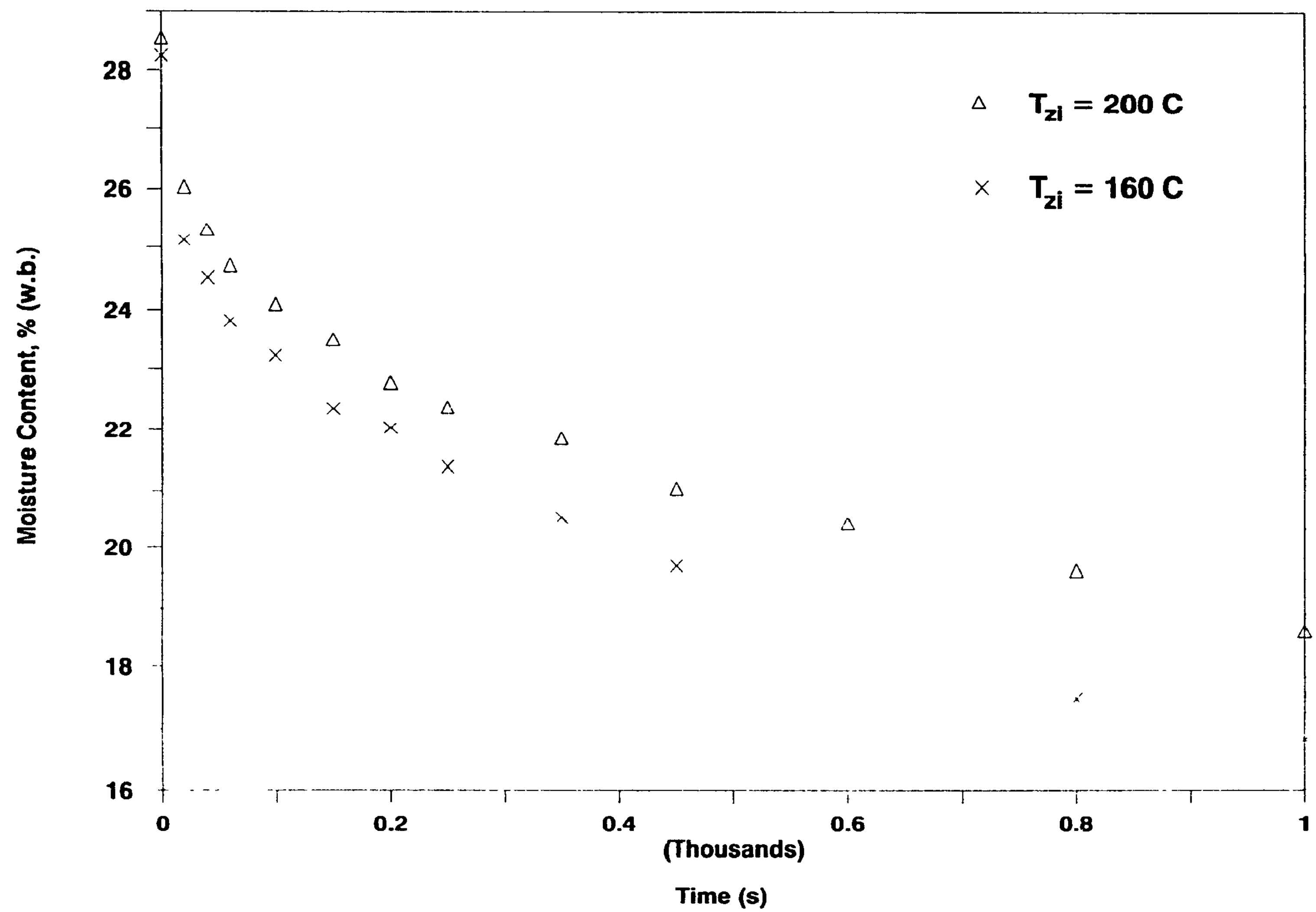


Fig. E1. Drying curves for corn